

Appendix A

### EMERGING TRANSPARENT CONDUCTING OXIDES FOR **ELECTRO-OPTICAL APPLICATIONS**

## CHARACTERISTICS OF EMERGING TCO MATERIALS

References	Wu, X.et al, JVST A 15(3),1997	Omata,T.et al Appl. Phys Lett 62 (5) 1993	Wu, X.et al, JVST A 15(3),1997	Yanagawa, K.et al Appl. Phys. Lett. 65(4) 1994	Appl. Phy. Lett 67(18)1995	Heiz,b.,OIC Topical Meeting, 1998
Film Thickness (nm)	530		290	170	·	140
Mobility (cm²/√¹s¹)	59.6		44.2	1.9	വ	37
Carrier Concentration (x10 <sup>20</sup> cm <sup>-3</sup> )	9.0	10	6.1	£. 7.	0.1	10
Resistivity (x10 <sup>-4</sup> Ωcm)	1.2	83	2.3	240	1000	1-2
Transmittance (%)	88		06	90	98 (Internal)	91
Material	CdSn <sub>2</sub> O <sub>4</sub>	CdGa <sub>2</sub> O <sub>4</sub>	Cdln <sub>2</sub> O <sub>4</sub>	CdSb <sub>2</sub> O <sub>6</sub> (Y)	Cd2GeO4	OTI

Appendix B

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### **EMERGING TRANSPARENT CONDUCTING OXIDES FOR ELECTRO-OPTICAL APPLICATIONS**

## CHARACTERISTICS OF EMERGING TCO MATERIALS

Material	Transmittance (%)	Resistivity (x10 <sup>-4</sup> Ωcm)	Carrier Concentration (x10 <sup>20</sup> cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /V <sup>-1</sup> s <sup>-1</sup> )	Film Thickness (nm)	References
ZnO(AI)	06	1.4	6.6	45	150	Imaeda, K.et al 43 <sup>rd</sup> AVS Symp. 1996
ZnO(Ga)	06	2.7	13	18	230	Imaeda, K.et al 43 <sup>rd</sup> AVS Symp. 1996
ZnSnO <sub>3</sub>	80	45	_	20	310	Minami, T.et al, JVST A 13(3) 1995
Zn <sub>2</sub> SnO <sub>4</sub>	92	929	0.058	19.0	620	Wu, X.et al, JVST A 15(3),1997
Zn <sub>2</sub> ln <sub>2</sub> O <sub>5</sub>	95	2.9	6.0	30	400	Minami, T.et al, Thin Solid Films 290-291, 1996
Zn <sub>3</sub> ln <sub>2</sub> O <sub>6</sub>	80	3.8	3.4	46	1400	Phillips, J.et al Appl. Phys. Lett. 67(15) 1995
170	91	1-2	10	37	140	Heiz,b.,OIC Topical Meeting, 1998

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# EMERGING TRANSPARENT CONDUCTING OXIDES FOR ELECTRO-OPTICAL APPLICATIONS

## CHARACTERISTICS OF EMERGING TCO MATERIALS

Material	Transmittance (%)	Resistivity (x10⁴Ωcm)	Concentration (x10 <sup>20</sup> cm <sup>-3</sup> )	Mobility (cm²/V <sup>-1</sup> s <sup>-1</sup> )	Thickness (nm)	References
MgIn <sub>2</sub> O <sub>4</sub>	85	20	1.8	15		Minami, T. et al, Thin Solid Films 270,1995
Mgln <sub>2</sub> O <sub>4</sub> - Zn <sub>2</sub> ln <sub>2</sub> O <sub>5</sub>	82	10	က	2	400	Minami, T.et al ICMC TF 1995
In <sub>2</sub> O <sub>3</sub> : Ga	85	5.8	5	20	400	Minami, 1.et al JVST A 15(3)1997
GalnO <sub>3</sub> (Sn,Ge)	06	29	4	10	1000	Phillips, J.et al Appl. Phys. Lett. 65(1) 1994
(Galn) <sub>2</sub> O <sub>3</sub>	06	10	က	20	100	Minami, T.et al JVST A 15(3)1997
ITO	91	1-2	10	37	140	Heiz,b.,OIC Topical Meeting, 1998

#### SOCIETY OF VACUUM COATERS

SHORT COURSE

ON

#### Deposition and Properties of ITO and Other Transparent Conductive Coatings

BY

Clark I. Bright
Delta V Technologies, Inc.

Appendix C

### DEPOSITION AND PROPERTIES OF ITO AND OTHER TRANSPARENT CONDUCTIVE COATINGS (TCC)

#### **OUTLINE (PART I)**

- FUNDAMENTALS OF CONDUCTIVITY AND THIN FILM OPTICS  $_{
  ho}$   $\lesssim$
- TCC FUNCTION AND PERFORMANCE IN APPLICATIONS
- MAJOR DEPOSITION METHODS FOR TCC
- IV. IMPORTANT PROCESS PARAMETER FOR TRANSPARENT CONDUCTIVE OXIDES (TCO)
- **DEVELOPING A TCO DEPOSITION PROCESS**
- TCC PROCESS EXAMPLES AND ASSOCIATED COATING PROPERTIES  $_{eta}$   ${f 8}{f \gamma}$

### DEPOSITION AND PROPERTIES OF ITO AND OTHER TRANSPARENT CONDUCTIVE COATINGS (TCC)

#### **OUTLINE (PART II)**

VII. STRATEGY FOR DEVELOPING A TCC TO MEET SPECIFIC APPLICATION REQUIREMENTS

VIII. APPLICATION EXAMPLES

SPECIFYING AND SELECTING COMMERCIALLY AVAILABLE TCC

X. ADVANCED TOPICS p. 111

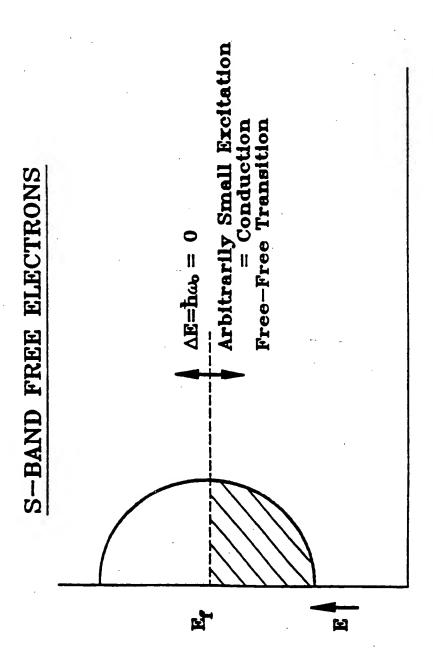
XI. QUESTIONS AND ANSWERS

## HISTORY OF TRANSPARENT CONDUCTIVE COATINGS

- FIRST TRANSPARENT CONDUCTIVE COATING (TCC) WAS CADMIUM OXIDE USED IN PHOTOVOLTAIC CELLS IN 1907
- IN THE 1940'S TIN OXIDE WAS DEPOSITED ON GLASS BY PYROLYSIS AND CHEMICAL VAPOR DEPOSITION
- IN THE 1950'S THIN METALS, e.g. GOLD, WERE VACUUM **EVAPORATED ON GLASS AND PLASTICS**
- IN THE 1970'S INDIUM OXIDE AND TIN DOPED INDIUM OXIDE (ITO) WERE MADE BY EVAPORATION AND DIODE SPUTTERING
- DEPOSIT ITO ON GLASS AND PLASTICS AT LOW TEMPERATURES WITH IN THE 1980'S MAGNETRON SPUTTERING MADE IT POSSIBLE TO GOOD PERFORMANCE
- TODAY MAJOR TCC USED IN DISPLAYS AND OTHER APPLICATIONS

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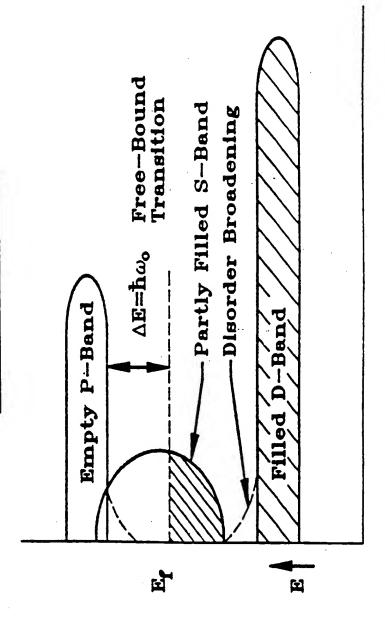
### METAL BAND STRUCTURE



Density of States --

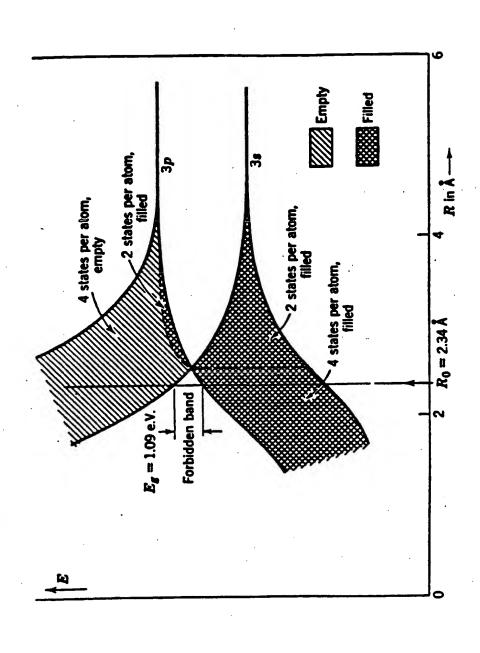
### METAL BAND STRUCTURE

#### REAL S-BAND METAL



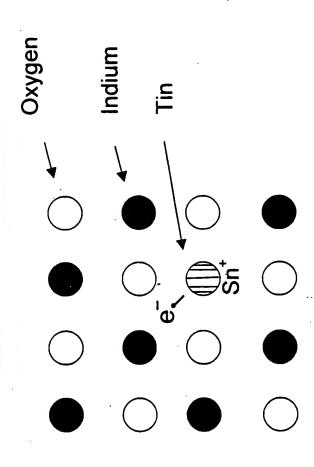
Density of States ---

## SEMICONDUCTOR BAND STRUCTURE



Energy Bands of Silicon as a Function of Nearest-Neighbor Distance (R)

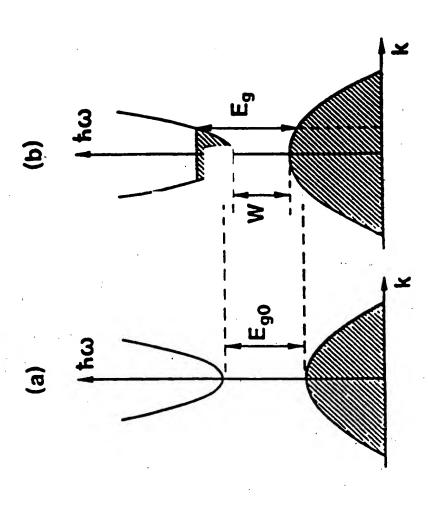
### CRYSTAL STRUCTURE



Simplified Crystal Structure and Doping Model for Indium Tin Oxide (C.G. Granqvist, <u>Spectrally Selective Surfaces for Heating and Cooling Applications</u>, TT 1 SPIE, 1989)

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#### BAND STRUCTURE



Assumed Band Structure for Undoped (a) and Tin Doped (b) Indium Oxide (C. G. Granqvist, Spectrally Selective Surfaces for Heating and Cooling Applications, TT 1, SPIE, 1989) Shaded Areas Indicate Occupied States

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### COPUPOD TORNATION

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

#### CONDUCTIVITY

METALS:  $\sigma(\omega) = j\omega\epsilon(\omega)$ 

AND FOR DC ( $\omega = 0$ )  $\sigma = N e \mu = N e^2 \tau = \omega_p^2 \tau$ 

N = NUMBER DENSITY OF ELECTRONS WHERE

e = ELECTRONIC CHARGE µ = ELECTRON MOBILITY

T = SCATTERING TIME

m = ELECTRON MASS $\omega_p = PLASMA FREQUENCY$ 

ω = ANGULAR FREQUENCY OF RADIATION

### SEMICONDUCTORS:

ELECTRONS AND HOLES. TCO ARE HIGHLY DEGENERATE n-TYPE SEMICONDUCTORS SO EXPRESSION FOR σ IS THE SAME AS FOR THE SAME FUNCTIONAL RELATIONS ARE DERIVED FOR BOTH **METALS** 

#### CONDUCTIVITY

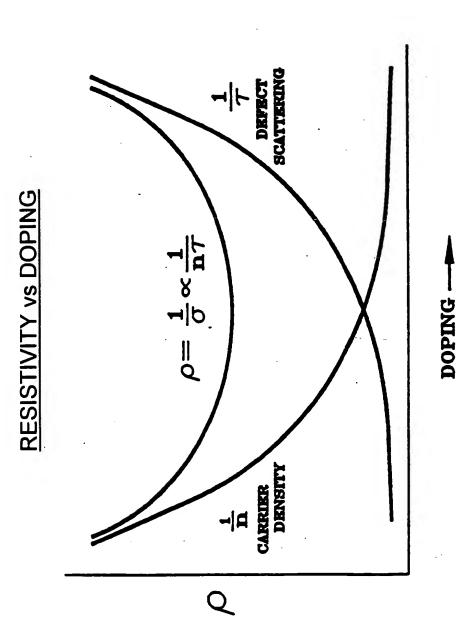
- (DENSITY) OF ELECTRONS AND THEIR MOBILITY (SCATTERING TIME) CONDUCTIVITY OF A METAL DEPENDS ONLY ON THE NUMBER
- FOR A SEMICONDUCTOR, THE CONDUCTION ELECTRONS ARE CREATED BY DOPING OR BY LACK OF STOICHIOMETRY
- CONDUCTION ELECTRONS ARE CREATED PRIMARILY BY OXYGEN FOR A TRANSPARENT CONDUCTING OXIDE (TCO), ITO et al, THE **DEFICIENCIES (VACANCIES)**
- THESE VACANCIES ARE CHARGE DEFECTS IN THE TCO LATTICE WHICH SCATTER ELECTRONS
- DOPING LEVEL AS WELL AS THE TCO CRYSTALLOGRAPHIC ORDER ELECTRON MOBILITY OR SCATTERING TIME DEPENDS ON THE

#### CONDUCTIVITY

- FOR A GIVEN TCO DEPOSITION PROCESS THERE IS A RESISTIVITY MUMINIM
- AT LOW DOPING LEVELS THE RESISTIVITY IS INCREASED BY LACK OF CONDUCTION ELECTRONS
- AT HIGH DOPING LEVELS THE RESISTIVITY IS INCREASED BY **ELECTRON SCATTERING FROM OXYGEN VACANCIES**
- THE MINIMUM RESISTIVITY OCCURS WHEN SCATTERING CAUSED BY **JOPING IS COMPARABLE TO SCATTERING FROM ALL OTHER**

### DASSOOR OSEROL

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS



### **ORIGIN OF RESISTIVIETY WELL**

### CARRIER ABSORPTION

- THE FREE CARRIERS NEEDED FOR CONDUCTION WILL ABSORB INCIDENT ELECTROMAGNETIC (EM) RADIATION
- ABSORPTION COEFFICIENT (a) VARIES WITH WAVELENGTH

$$\alpha = 4 \pi k$$
 WHERE k IS THE EXTINCTION COEFFICIENT AND  $\lambda$  IS THE WAVELENGTH

METALS AND SEMICONDUCTOR HAVE CHARACTERISTIC SPECTRAL OPTICAL PROPERTIES

#### DRUDE THEORY

THE DIELECTRIC FUNCTION FOR CONDUCTION (FREE) ELECTRONS:

$$\varepsilon(\omega) = \varepsilon_1 - i\varepsilon_2 = n^2 \text{ AND } n = n - ik \text{ THEN } \varepsilon_1 = n^2 - k^2 \text{ AND } \varepsilon_2 = 2nk$$

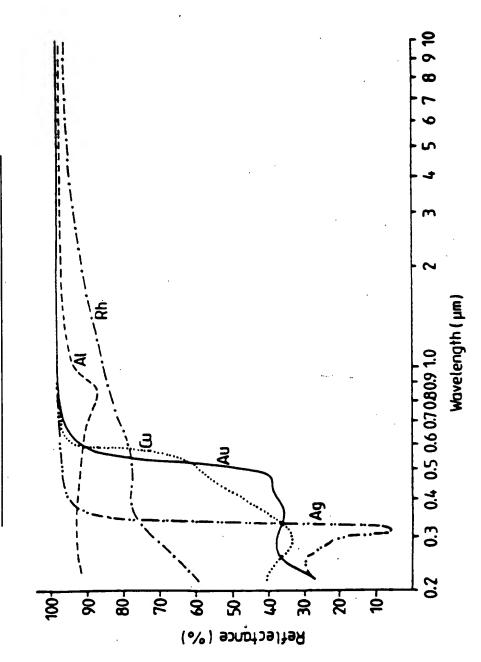
AND 
$$\varepsilon_1 = 0$$
 WHEN  $\omega = \omega_p$  AND  $\omega_p^2 =$ 

WHERE 
$$n = \text{NUMBER DENSITY OF ELECTRONS}$$
 $e = \text{ELECTRONIC CHARGE}$ 
 $\tau = \text{SCATTERING TIME}$ 
 $m = \text{ELECTRON MASS}$ 
 $\omega_p = \text{PLASMA FREQUENCY}$ 
 $\omega_p = \text{ANGULAR FREQUENCY OF RADIATION}$ 

METAL NITRIDES:

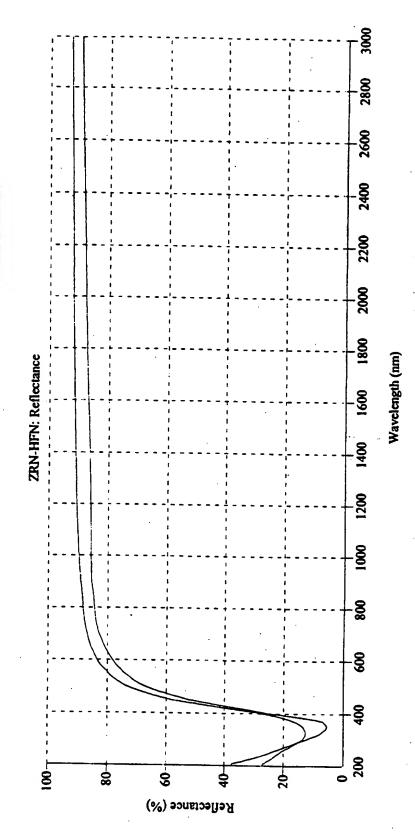
$$\varepsilon(\omega) = \varepsilon_1(\infty) - (\omega_p^2 / \omega^2 + i\omega/\tau)$$
 AND  $\omega_p^2 = N e^2 - \varepsilon_0 m^*$ 

### **OPTICS OF METALLIC THIN FILMS**



Change in Reflectance at Plasma Wavelength for Simple Metals (Au, Ag, Cu) (From G. Hass, J. Opt. Soc. Am. 45, 945-52, 1955)

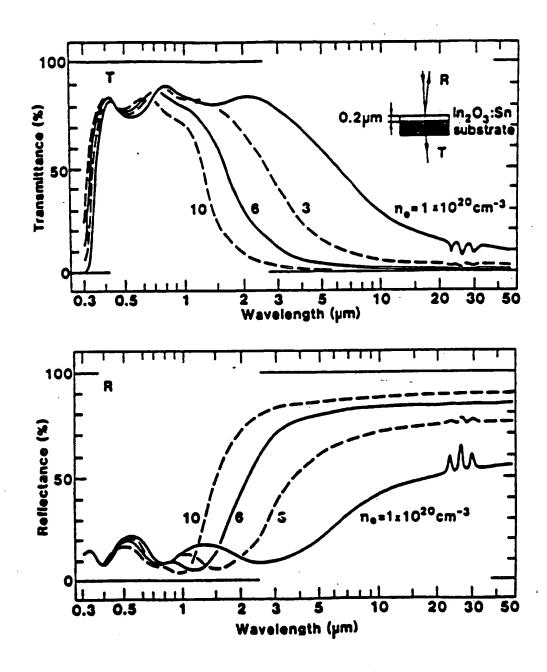
## **OPTICS OF METALLIC NITRIDE THIN FILMS**



### Change in Reflectance at Plasma Wavelength for HfN, ZrN HfN - lower trace, ZrN - upper trace

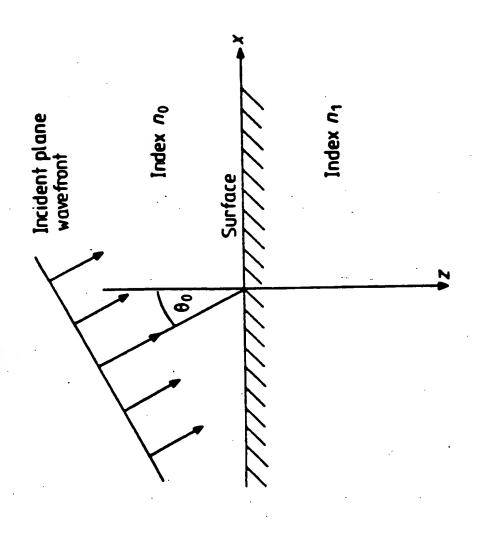
(Calculated from optical constants in E.D. Palik, Ed. Handbook of Optical Constants of Solids III)

#### CONDUCTIVITY



Spectral Properties of ITO as a Function of Carrier Density (Ne) (From, J. App. Opt, 24, 12 15june 1985)

#### THIN FILM OPTICS



Plane Wave Incident on a Single Surface (From Thin Film Optical Filters, H. A. Macleod, Macmillan, 1968)

#### THIN FILM OPTICS

## REFLECTANCE OF SINGLE SURFACE

EX: FOR nFILM = 2.0 and nMEDIUM = 1.0 (AIR)

$$R = \frac{1-2}{1+2}^2 = 0.11111 = 11.1\%$$
 (PER SURFACE)

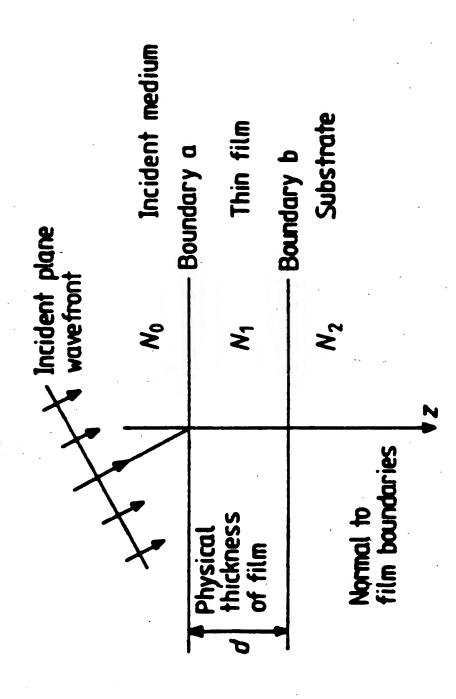
EX: FOR  $n_{FILM} = 1.51$  and  $n_{MEDIUM} = 1.0$ .

$$R = \underbrace{1 - 1.51}_{1 + 1.51}^{2} = 0.0413 = 4.1\% \text{ (PER SURFACE)}$$

EX: FOR  $n_{FILM} = 2.0$  and  $n_{SUB} = 1.51$ 

$$R = \frac{n_{SUB} - n_{FILM}}{n_{SUB} + n_{FILM}}^2 = \frac{1.51 - 2.0}{1.51 + 2.0}^2 = 0.0195 = 1.95\%$$

#### THIN FILM OPTICS



Plane Wave Incident on a Thin Film (From Thin Film Optical Filters, H. A. Macleod, Macmillan, 1968)

#### THIN FILMS OPTICS

- OPTICAL THICKNESS IS THE PRODUCT OF INDEX OF REFRACTIONS AND PHYSICAL THICKNESS = n x d (WAVES)
- QUARTERWAVE OPTICAL THICKNESS =  $n \times d = \underline{\lambda}$

EX: FOR n = 2 AND d = 100 NM

$$\lambda_{\chi} = 4 \text{ nd} = 800 \text{ NM}$$

HALFWAVE OPTICAL THICKNESS =  $n \times d = \underline{\lambda}$ 

EX: FOR 
$$n = 2$$
 AND  $d = 100$  NM

$$\lambda_{\%} = 2 \text{ nd} = 400 \text{ NM}$$

### COPULOR COUNTRY

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

#### THIN FILM OPTICS

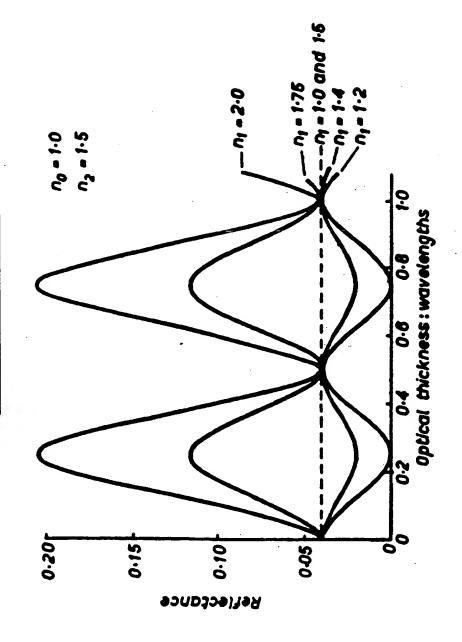
## SINGLE LAYER ON A SUBSTRATE

RM IS EITHER A MAXIMUM OR A MINIMUM IF THE OPTICAL THICKNESS IS AN ODD MULTIPLE OF A QUARTERWAVE, e.g.  $\lambda$ ,  $3\lambda$ ,  $5\lambda$ , etc 4 4 4

EX: FOR  $n_{FILM} = 2.0$ ,  $n_{SUB} = 1.51 \text{ AND } n_0 = 1.0$ 

$$R_M = 4 - 1.51$$
 = 0.2042 = 20.42%  $4 + 1.51$ 

#### THIN FILM OPTICS



Variation of reflectance (at air side) with thickness for films of various refractive indices on a substrate of index 1.5

(From O.S. Heavens, Optical Properties of Thin Solid Films, Dover, 1985)

#### THIN FILMS

### SURFACE RESISTIVITY

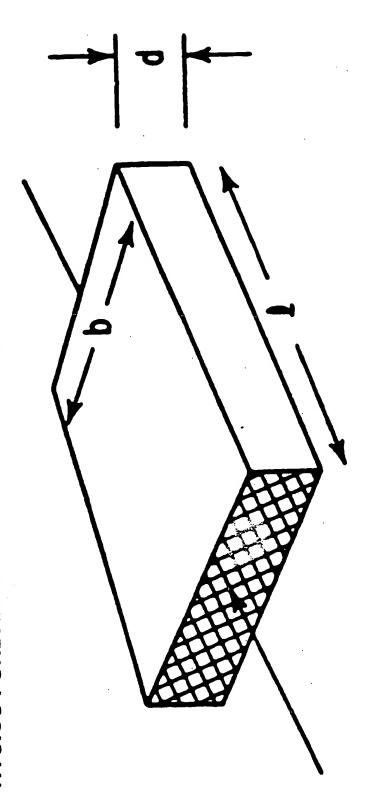
CONDUCTIVITY IS RECIPROCAL OF VOLUME RESISTIVITY (p)

$$\rho = \frac{1}{2} OHM - CM$$

- THIN FILMS ARE OFTEN INHOMOGENEOUS, CONTAIN DEFECTS, CAN EXHIBIT SURFACE SCATTERING, AND FILM THICKNESS IS DIFFICULT HOWEVER, VOLUME RESISTIVITY CAN BE MISLEADING BECAUSE TO MEASURE ACCURATELY
- THEREFORE SURFACE (SHEET) RESISTIVITY (r) IS USED

### TOPESOL BOOKEDL

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS



### SURFACE RESISTIVITY

$$R = \frac{p \times \ell}{b \times d}$$

$$R = \frac{p \times \ell}{d} = \frac{r \times \ell}{b}$$

$$R \times \frac{p}{l} = \frac{r \times \ell}{b}$$

BECAUSE WHEN ( = b, 1.e., ON A SQUARE AREA, THE SURFACE RESISTIVITY EQUALS THE MEASURED RESISTANCE, r = R (OHMS)

#### THIN FILMS

### SURFACE RESISTIVITY

- NOTE THAT THE MEASURED VALUE OF r IS INDEPENDENT OF THE SIZE OF THE SQUARE (AREA)
- IT IS ONLY DEPENDENT ON THE GEOMETRIC RATIO OF WIDTH TO LENGTH (b/l)
- THUS A SQUARE INCH OR A SQUARE METER OF COATING WILL HAVE THE SAME RESISTANCE

#### THIN FILMS

### SURFACE RESISTIVITY

COMPARE THE THEORETICAL COATING THICKNESSES (BULK MATERIAL) OF TWO 10 OHMS/SQUARE THIN FILMS:

r = p = 10 OHMS/SQAURE $\rho = 2.4 \times 10^{-6} \text{ OHM-CM}$  $d = p = 2.4 \times 10^{-7} \text{ CM}$ d = 2.4 NM $\rho = 2 \times 10^{-4} \text{ OHM-CM}$   $r = \frac{10}{d} = 10 \text{ OHMS/SQUARE}$  $d = p = 2 \times 10^{-5} \text{ CM}$ d = 200 NMFOR

THUS FOR THE SAME OHMS/SQUARE, SEMICONDUCTOR TCC ~ 100X THICKER THAN METALLIC TCC

#### OPTICS

SPECTRAL VALUES

TRANSMITTANCE IS T(A), REFLECTANCE R(A), ABSORPTANCE A(A)

 $T(\lambda) + R(\lambda) + A(\lambda) = 1$ 

INTEGRATED VALUES:

AVERAGE - e.g. T AVERAGE =

WAVELENGTHS (INTERNALS) WHERE M IS NUMBER OF

**EYE WEIGHTED - LUMINOUS T** 

 $\sum T(\lambda) \Delta \lambda$ A = 700NM11

T(A) dA

**MN002 = Y** 

M Δλ λ = 400NM

A = 780NM

A = 780NM

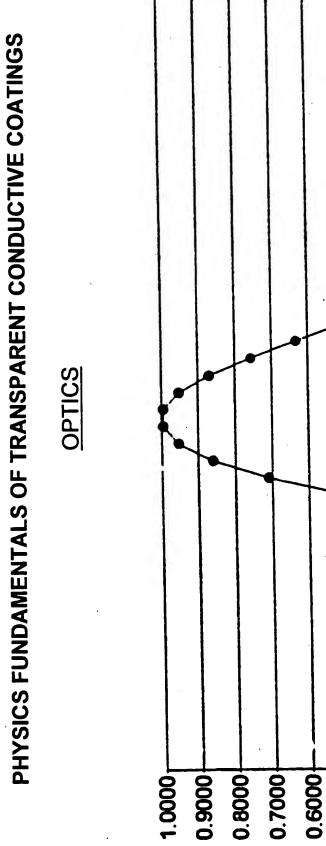
 $= \sum \frac{T(\lambda)K(\lambda)P(\lambda)\Delta(\lambda)}{P(\lambda)K(\lambda)\Delta(\lambda)}$  $T(\lambda)K(\lambda)P(\lambda)d(\lambda)$  $P(\lambda)K(\lambda)d(\lambda)$ 

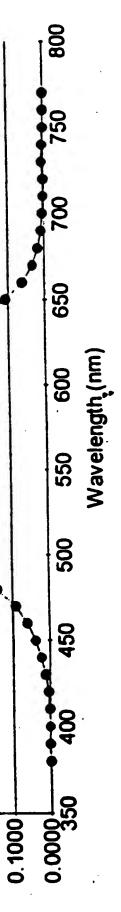
A = 380NM

 $\lambda = 380 \text{NM}$ 

WHERE P(A) IS AVERAGE DAYLIGHT AND K(A) IS RELATIVE SENSITIVITY OF PHOTOPIC ADAPTED EYE

"VISIBLE" - NOT DEFINED GENERALLY, OFTEN MEANS LUMINOUS





0.2000

0.3000

0.5000

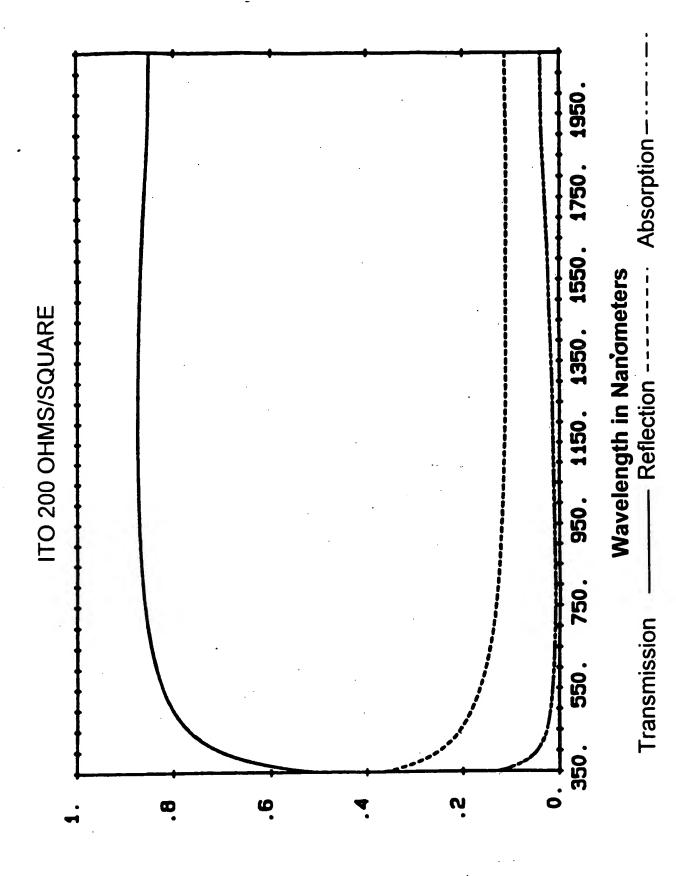
0.4000

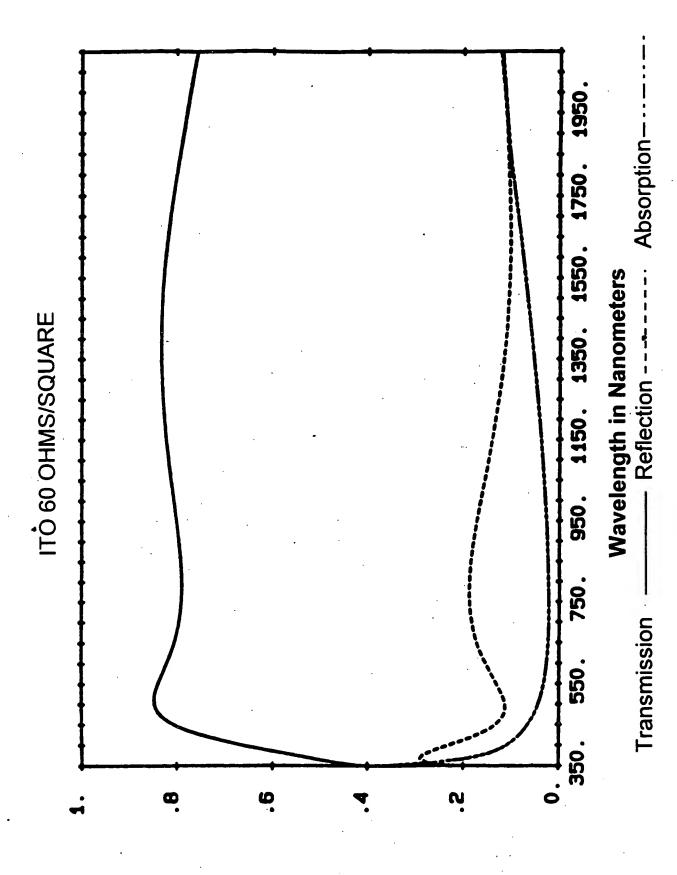
#### COLOR

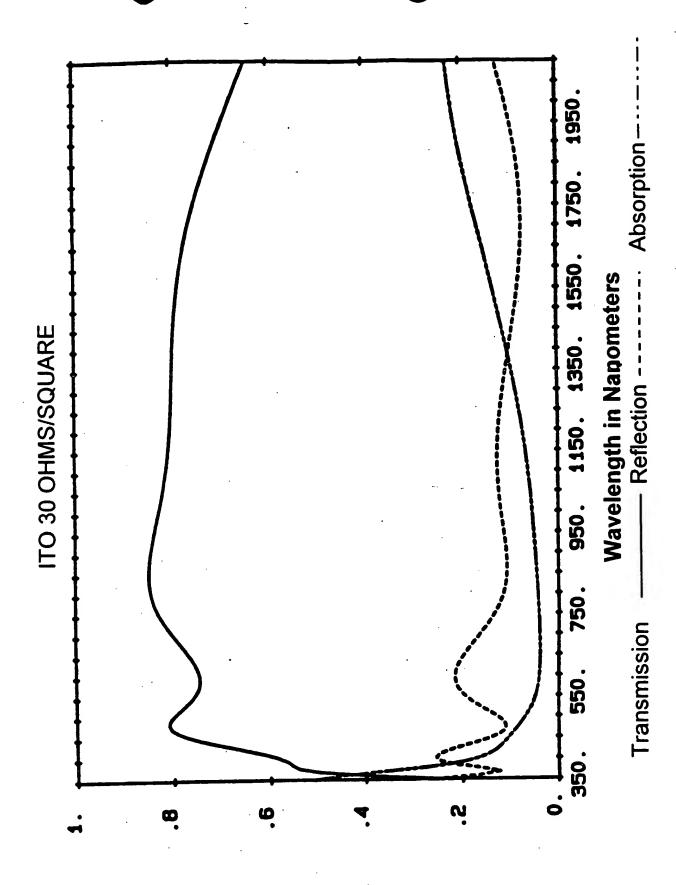
4 <sup>th</sup> Order t(Å)		5000	5550	2800	0909	6300
3 <sup>rd</sup> Order t(Å)		3600	4000	4300	4600	4800
2 <sup>nd</sup> Order t(Å)		2100	2500	2850	3100	3350
1 <sup>ST</sup> Order t(Å)	75 230 380 620	770	1400	1600	1750	1900
Color	Gray Tan Brown	Violet	Green	Yellow	Orange	Red

 $<sup>^{</sup>a}n = 2.00.$ 

Colors of TCO Thin Films When Viewed in Reflected White Light. (From J.L. Vossen, Physics of Thin Films, Vol. 9, Academic Press, 1997)

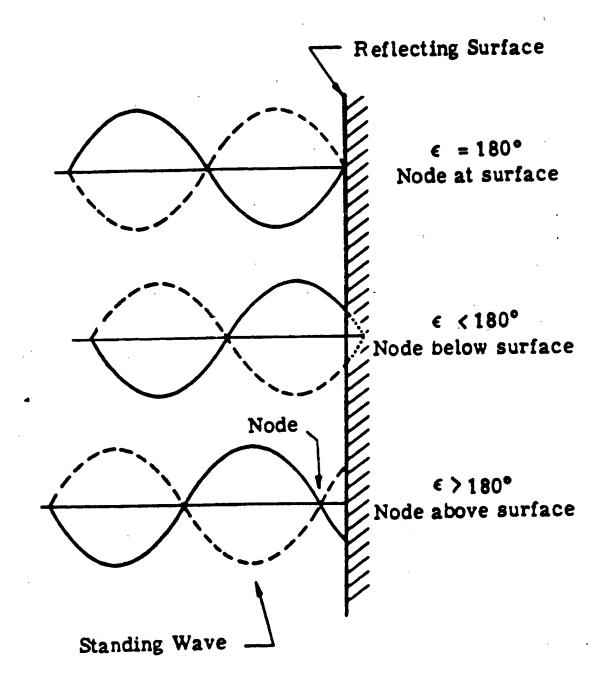






#### PHYSICS FUNDAMENTAL OF TRANSPARENT CONDUCTIVE COATINGS

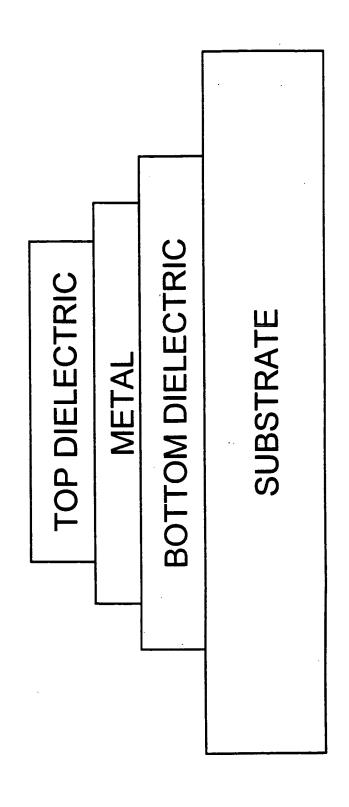
#### Thin Film Optics

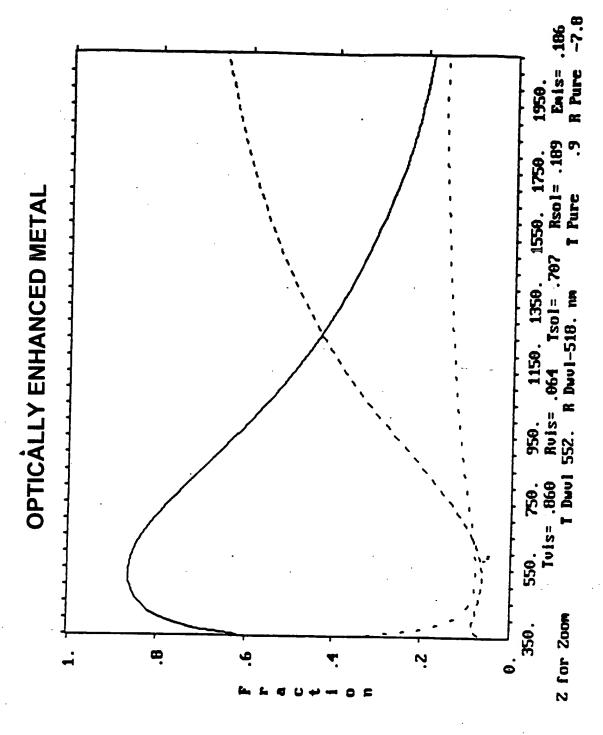


Phase Shift upon Reflection and Standing Wave (From Mil, Std. Handbook, Optical Design, Mil – Hdbk – 141, 1962)

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

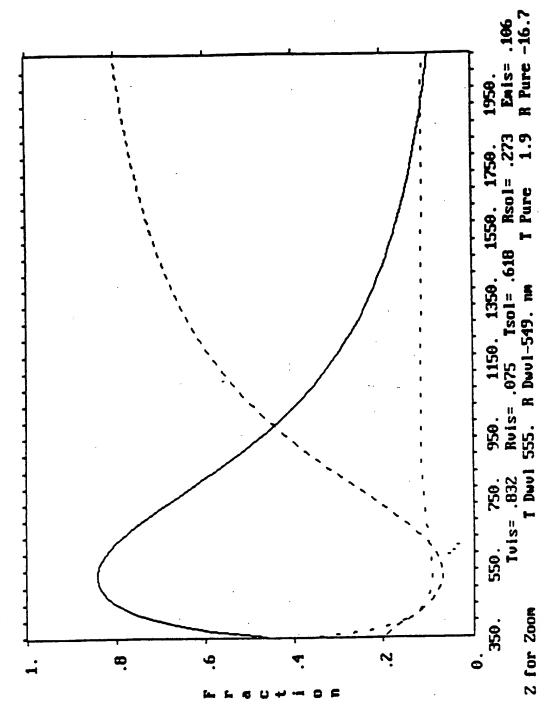
#### THIN FILM OPTICS



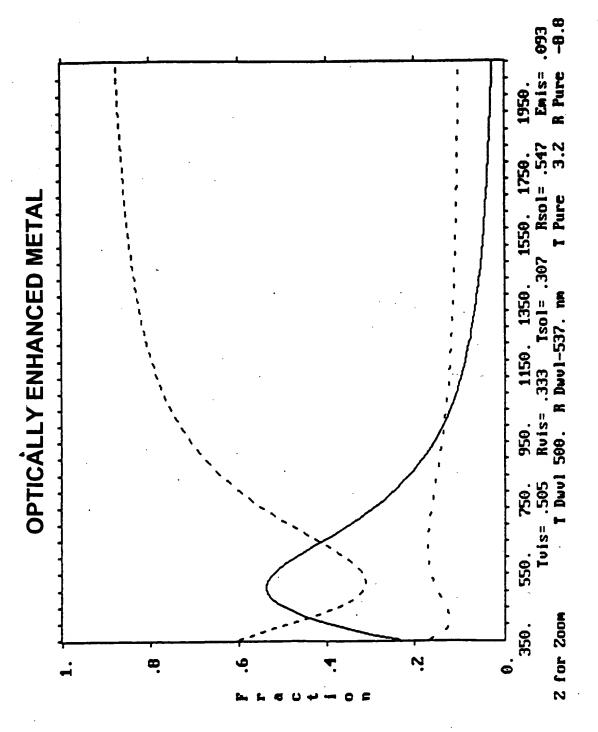


Metal Oxide – Silver – Metal Oxide Coating on PET, 20 Ohms/Square Transmittance – upper trace, Reflectance – middle trace, Aborptance – lower trace

### **OPTICALLY ENHANCED METAL**



Metal Oxide - Silver - Metal Oxide Coating on PET, 10 Ohms/Square Transmittance - upper trace, Reflectance - middle trace, Aborptance - lower trace



Metal Oxide - Silver - Metal Oxide Coating on PET, 5 Ohms/Square Transmittance - upper trace, Reflectance - middle trace, Aborptance - lower trace

# PHYSICS FUNDAMENTALS OF TRANSPARENT CONDUCTIVE COATINGS

## OPTICAL AND ELECTRICAL PERFORMANCE

- A COMPROMISE BETWEEN HIGH OPTICAL TRANSMITTANCE AND HIGH CONDUCTIVITY (LOW RESISTIVITY) IS ALWAYS REQUIRED
- OPTICAL TRANSMITTANCE IS FUNDAMENTALLY LIMITED BY **ABSORPTION**
- OPTICAL TRANSMITTANCE AND REFLECTANCE ARE WAVELENGTH DEPENDENT
- i.e. METAL OR SEMICONDUCTOR) AND WAVEBAND (UV, VIS, NEAR OPTICAL PERFORMANCE CAN BE GENERALIZED BY TYPE OF TCC R, MIDWAVE IR AND LONGWAVE IR)
- MANY FIGURES-OF-MERIT FOR TCC HAVE BEEN DEFINED BUT LIMITED USEFULNESS BECAUSE NEED TO BE APPLICATION

# SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

#### **FUNCTION**

TRANSPARENT ELECTRODE:

- REQUIREMENT IS TO APPLY AN ELECTRICAL FIELD
- THEREFORE, COMPROMISE IS FOR HIGH TRANSMITTANCE WITH LOW CONDUCTIVITY (HIGH RESISTIVITY)

## ELECTROMAGNETIC INTERFERENCE SHIELD:

- REQUIREMENT IS TO REFLECT EM WAVES WITH SPECIFIED **FREQUENCIES**
- SHIELDING EFFECTIVENESS IS INVERSELY PROPORTIONAL TO SURFACE RESISTIVITY, i.e., LOW OHMS/SQUARE GIVES HIGH SHIELDING
- COMPROMISE IS FOR LOW RESISTIVITY WITH ACCEPTABLE **TRANSMITTANCE**

# SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

#### **FUNCTION**

#### HEATER:

- REQUIREMENT IS FOR A RESISTANCE WHICH PERMITS ACHIEVING THE NEEDED POWER (DENSITY) FROM THE AVAILABLE VOLTAGE SOURCE
- CHOICE OF VOLTAGE SOURCE i.e. MORE THAN ONE OHMS/SQUARE CAN TRANSMITTANCE CAN BE MAXIMIZED BY USE OF PART GEOMETRY AND MEET RESISTANCE REQUIREMENT

#### **ANTISTATIC:**

- REQUIREMENT IS TO DISCHARGE STATIC CHARGE NON-DESTRUCTIVELY
- RESISTANCE CAN BE HIGH AND STILL ACHIEVE ADEQUATE DISCHARGE **LIMES**
- **IHUS, OHMS/SQUARE CAN BE HIGH, WITH ATTENDANT HIGH IRANSMITTANCE**

# SPECIFYING AND SELECTING TRANSPARENT CONDUCTIVE COATINGS

#### **FUNCTION**

#### **HEAT MIRROR:**

- REQUIREMENT IS FOR HIGH SOLAR REFLECTANCE, LOW INFRARED (IR) EMISSIVITY AND MEDIUM LUMINOUS TRANSMITTANCE
- HIGH FREE CARRIER DENSITY PRODUCES HIGH SOLAR AND INFRARED REFLECTANCE
- PLASMA FREQUENCY SHOULD IDEALLY BE AT EDGE OF **VISIBLE/NEAR IR WAVEBANDS**

### CONDUCTIVE ANTIREFLECTION

- OPTICAL REQUIREMENT IS FOR LOW LUMINOUS REFLECTANCE AND LOW AVERAGE VISIBLE REFLECTANCE
- CONDUCTIVE REQUIREMENTS IS FOR ANTISTATIC AND/OR ELECTROMAGNETIC INTERFERENCE SHIELDING
- **OPTICAL DESIGN DETERMINES TCC THICKNESS**

#### **EVAPORATION**

#### THERMAL:

- REFRACTORY METAL BOATS, OR FILAMENTS AND FROM CERAMIC NOBLE METALS (Ag, Au) AND TCO LIKE INDIUM OXIDE (10), INDIUM I'IN OXIDE (ITO) AND TIN OXIDE (TO) CAN BE DEPOSITED FROM CRUCIBLES
- TYPICAL STARTING MATERIALS ARE METAL WIRES AND PIECES OR METAL OXIDE POWDERS (CHUNKS) AND PELLETS
- **THE DIFFICULTY AND TEMPERATURE FOR EVAPORATION** INCREASES WITH THE MATERIAL MELTING POINT
- OXYGEN BACKGROUND GAS USED FOR REACTIVE EVAPORATION OR TO MAKE UP FOR DISSOCIATION OF METAL OXIDES

#### DYSUSCION . DESCY

# TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

#### **EVAPORATION**

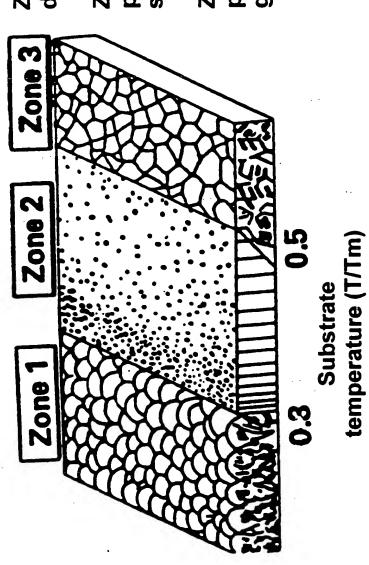
#### ELECTRON - BEAM:

- BOTH METALS AND METAL OXIDES CAN BE READILY EVAPORATED
- IO, ITO OR TO DEPOSITED WITH EQUAL EASY
- OXYGEN GAS USED FOR REACTIVE EVAPORATION OR TO MAKE UP FOR DISSOCIATION OF METAL OXIDES

### PLASMA OR ION ASSISTED

- DEPOSITION RATES CAN BE INCREASED
- FILM DENSITY AND REFRACTIVE INDEX INCREASED

## MICROSTRUCTURES OF EVAPORATED COATINGS



Zone 1: Porous, Low density, brittle coating.

Zone 2: Surface diffusion produces dense, columnar structure

Zone 3: Bulk diffusion produces recrystallized grains

B.A. Movchan and A.V. Demshishin, Fiz. Metal. Metalloved., 28, part 2:83 (1969)

#### SPUTTERING

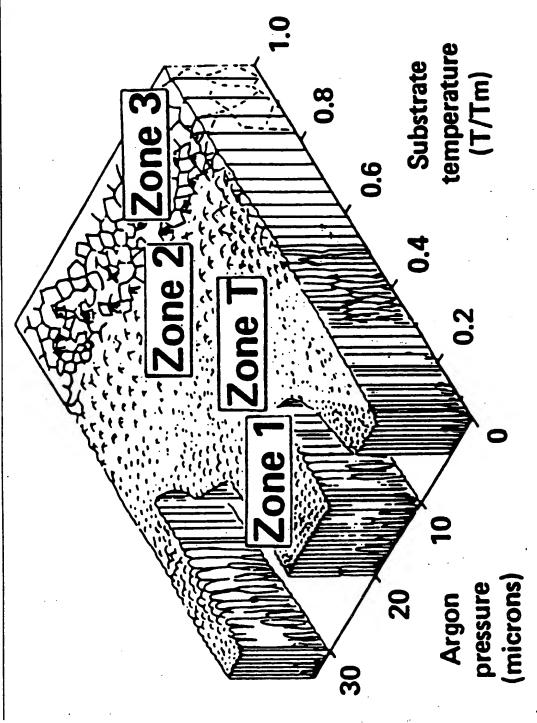
DC MAGNETRON - METALS

HIGH DEPOSITION RATES

**DENSE FILMS** 

BULK LIKE REFRACTIVE INDEX

## THORNTON STRUCTURE ZONE MODEL FOR SPUTTERED COATINGS



from J.A. Thornton, J. Vac. Sci. Trchnol; 11:666 (1974)

#### SPUTTERING

### DC MAGNETRON - REACTIVE

- REACTIVE SPUTTERING FROM METALLIC TARGETS TO DEPOSIT 10, ITO; TO, ZINC OXIDE (ZO) ET AL
- HIGH DEPOSITION RATE IF TARGET IS KEPT FROM OXIDIZING
- ARCING AT OXIDIZED AREAS OF TARGET IS A PROBLEM

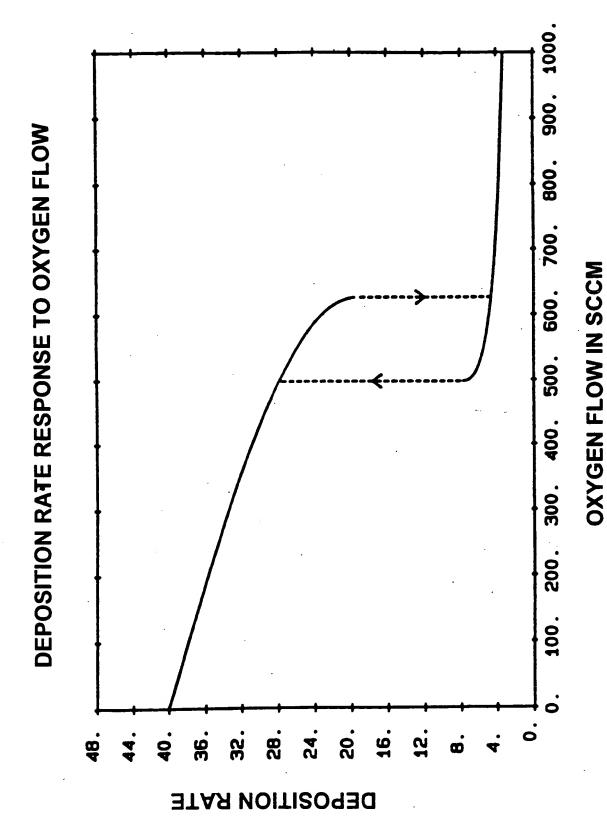
900. 1000. 800. PRESSURE RESPONSE TO OXYGEN FLOW 500. 600. 700. 300. 100. 200.

**PRESSURE** 

3

**OXYGEN FLOW IN SCCM** 

COPUCACO COPUCACO



COATING OXYGEN/METAL RATIO RESPONSE TO OXYGEN FLOW 900. 800. 700. **OXYGEN FLOW IN SCCM 600**. 500. 400. 300. 200. 100 1.6 COATING OXYGEN//METAL RATIO

#### SPUTTERING

### DC MAGNETRON - SEMIREACTIVE

- SEMIREACTIVE SPUTTERING FROM CERAMIC TARGETS OF REDUCED IO, ITO, TO, ZO
- MUCH EASIER TO CONTROL THAN REACTIVE METAL PROCESS
- ARCING PROBLEM AND COATING DEFECTS REDUCED
- REQUIRES HIGHER POWER (DENSITY) THAN METAL TARGET FOR **EQUIVALENT SPUTTERING RATES**

#### SPUTTERING

## RF SPUTTERING - DIODE OR MAGNETRON

- MAIN BENEFIT IS THAT TARGET MATERIALS NEED NOT HAVE DC CONDUCTIVITY
- MAIN DISADVANTAGE IS LOW DEPOSITION RATES
- **EM SHIELDING OF EQUIPMENT REQUIRED**
- SAFETY ISSUES

#### HOTHOUGH BOOKED

## TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

## PYROLYSIS AND CHEMICAL VAPOR DEPOSITION (CVD)

PYROLYSIS - LIQUID

CAN USE LOW COST MATERIALS

MATERIALS AND REACTION PRODUCTS CAN BE HAZARDOUS

DEPOSITION POSSIBLE AT ATMOSPHERIC PRESSURE

TYPICALLY SPRAY PROCESS

HIGH TEMPERATURE PROCESS

### POST DEPOSITION PROCESSES

#### TCO POST PROCESSING

- BAKING IN VACUUM CAN REDUCE RESISTIVITY, IMPROVE CRYSTALLINITY, REDUCE INTRINSIC COATING STRESS
- BAKING IN OXIDIZING GAS CAN REDUCE ABSORPTION, INCREASE TRANSMITTANCE, IMPROVE DURABILITY, INCREASE RESISTIVITY, INCREASE REFRACTIVE INDEX
- BAKING IN AN INERT GAS CAN INCREASE REACTIVE INDEX, REDUCE COATING STRESS AND IMPROVE CRYSTALLINITY
- CRYSTALLINITY, REDUCE COATING STRESS, LOWER REFRACTIVE INDEX BAKING IN A REDUCING GAS CAN LOWER RESISTIVITY IMPROVE AND INCREASE ABSORPTION

#### Coemocoo Coemoco

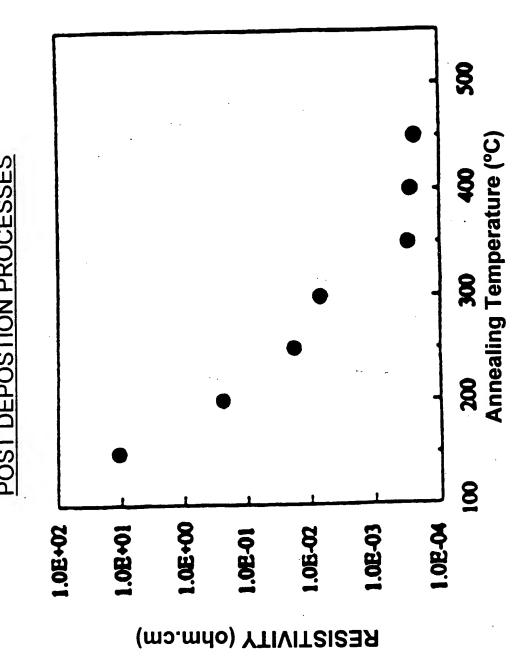
## TRANSPARENT CONDUCTIVE COATING DEPOSITION METHODS

## PYROLYSIS AND CHEMICAL VAPOR DEPOSITION (CVD)

### **LOW PRESSURE CVD - VAPOR**

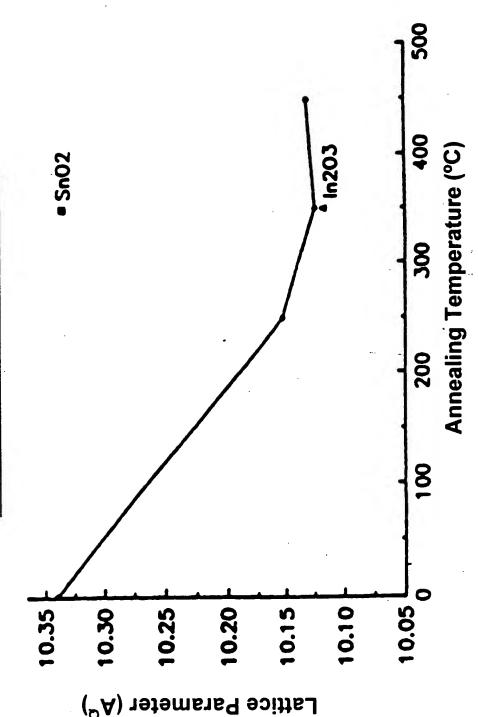
- COATS ALL EXPOSED SURFACES
- COATINGS ARE VERY DURABLE
- DEPOSITION RATES CAN BE VERY HIGH
- MATERIALS AND REACTION PRODUCTS CAN BE HAZARDOUS
- HIGH TEMPERATURE PROCESS
- PLASMA ENHANCEMENT CAN REDUCE PROCESS TEMPERATURE

### POST DEPOSTION PROCESSES



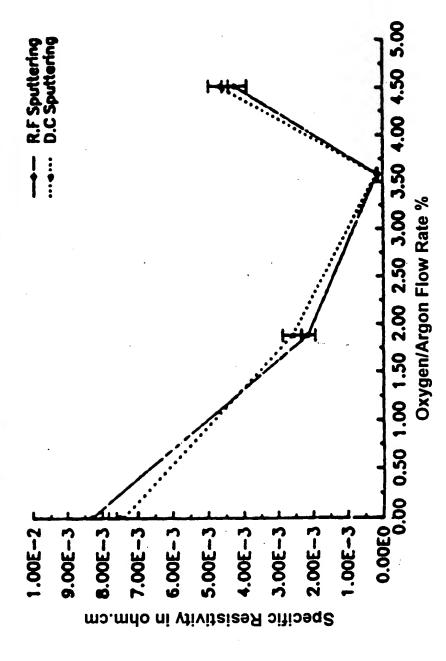
Surface Resistivity Versus Vacuum Annealing Temperature (25 min.) for Sputtered ITO (From M. A. Martines, et al. Thin Solid Films. 269, (1995) 80-84)

### POST DEPOSTION PROCESSES



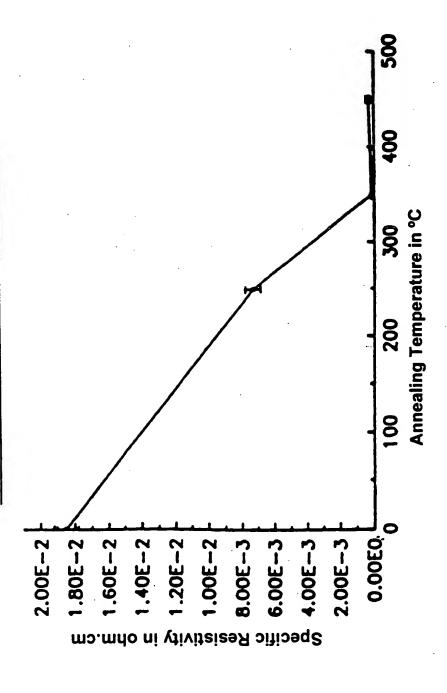
Surface Resistivity Versus Annealing Temperature (24 min.) for Sputtered ITO (From M. A. Martines, et al. <u>Thin Solid Films</u>, 269, (1995) 80-84)

### POST DEPOSITION PROCESSES



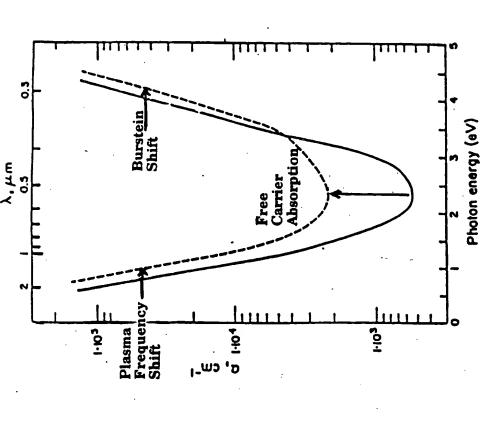
Surface Resistivity for Sputtered ITO Films Annealed (2 hours in air) at 350°C as a Function of Oxygen/Argon Flow Rate during Sputtering (From R. N. Joshi, et al. Thin Solid Films, 257, (1995) 32-35)

### POST DEPOSITION PROCESSES



Surface Resistivity Versus Annealing Temperature (2 hours in air) for r.f. Sputtered ITO (From R. N. Joshi, et al, Thin Solid Films, 257, (1995) 32-35)

Absorption as a Function of Photon Energy



Solid line: As deposited ITO film. (N =  $5.8 \times 10^{20} / \text{cm}^3$ ) Broken line: After 30 min. at 400 C in N<sub>2</sub> + 10% H<sub>2</sub>. (N =  $11.2 \times 10^{20}$  /cm<sup>3</sup>)

## IMPORTANT TCO VACUUM PROCESS PARAMETERS

### SUBSTRATE TEMPERATURE

- CRYSTALLINITY WHICH INCREASE ELECTRON MOBILITY AND MAXIMIZING SUBSTRATE TEMPERATURE WILL IMPROVE SCATTERING TIME
- A THRESHOLD TEMPERATURE IS REQUIRED TO ACTIVATE METAL, e.g. Sn, DOPANTS

#### **DEPOSITION RATE**

- LOW PRODUCT COST DICTATES HIGH DEPOSITION RATES
- FOR SPUTTERING, HIGH RATES REQUIRES OPERATING IN THE METAL MODE
- HIGH DEPOSITION RATES MUST BE SUPPORTED BY HIGH REACTION RATES BETWEEN METAL ATOMS OR IONS AND OXYGEN ATOMS OR IONS

## IMPORTANT TCO VACUUM PROCESS PARAMETERS

### **OXYGEN PARTIAL PRESSURE**

BECAUSE OXYGEN DEFICIENCY IS THE MAJOR CONTROL OF CONDUCTIVITY AND ABSORPTION, CONTROL IS CRITICAL

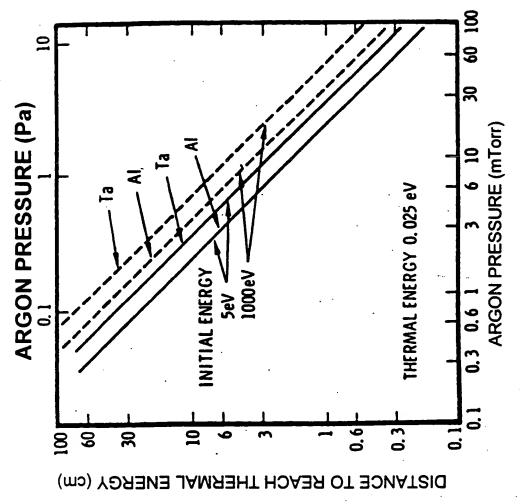
#### CHAMBER PRESSURE

- LOWER CHAMBER PRESSURE MEANS ATOMS ARRIVE AT SUBSTRATE WITH MORE KINETIC ENERGY WHICH IMPROVES **CRYSTALLINIETY AND REDUCES DEFECTS**
- IF PRESSURE IS TOO LOW, DEPOSITED FILM WILL BE REDUCED (METALLIC)
- IF PRESSURE IS TOO LOW, A SPUTTERING PROCESS CAN NOT BE **MAINTAINED**
- LOW CHAMBER PRESSURE PRODUCES MORE LINE-OF-SIGHT

## IMPORTANT TCO VACUUM PROCESS PARAMETERS

### SOURCE TO SUBSTRATE DISTANCE

- SMALL SEPARATION PRODUCES MORE SUBSTRATE HEATING
- SMALL SEPARATION MEANS ATOMS AND IONS ARRIVE WITH MORE KINETIC ENERGY
- LARGE SEPARATION PRODUCES MORE LINE-OF-SIGHT DEPOSITION
- LARGE SEPARATION ALLOWS MORE TIME FOR REACTION WITH **OXYGEN IN CHAMBER**



different initial energies are thermalized in Ar at various pressures. Thermalized Maximum distance from the target at which sputtered Al and Ta atoms of energy assumed to be 0.025 eV

W.D. Westwood, <u>J. Vac. Sci. Technol.</u> 15, 188 (1978).

### **DEVELOPING AN ITO PROCESS**

## SELECTING THE DEPOSITION PROCESS

- DEPOSITION PROCESS MAY BE DICTATED BY AVAILABLE EQUIPMENT
- COATING APPLICATION MAY FAVOR A PARTICULAR DEPOSITION **TECHNOLOGY**
- TYPE OF SUBSTRATE CAN INFLUENCE DEPOSITION PROCESS CHOICE
- COATING DENSITY AND DURABILITY MAY INFLUENCE PROCESS CHOICE

# STARTING MATERIAL CHOICE

- AFTER DEPOSITION PROCESS IS CHOSEN, STARTING MATERIAL CHOICES ARE REDUCED
- COST/PERFORMANCE CONSIDERATION
- CONVENIENCE AND AVAILABILITY ISSUES
- APPLICATION REQUIREMENTS USUALLY MAJOR FACTOR IN SELECTING TYPE AND FORM OF STARTING MATERIAL

# CHOOSING SUBSTRATE TEMPERATURE

- FROM COATING PERFORMANCE CONSIDERATIONS ALONE -"HOTTER IS BETTER"
- EQUIPMENT LIMITATIONS MAY DICTATE MAXIMUM TEMPERATURE
- THERMAL LIMITATIONS OF SUBSTRATE MAY DETERMINE PROCESS **TEMPERATURE**
- COST/PERFORMANCE TRADE-OFFS CAN INFLUENCE TEMPERATURE SELECTION

## **SELECTING ITO THICKNESS**

- ITO THICKNESS RANGE USUALLY DETERMINED BY COATING **FUNCTION**
- **OPTICAL REQUIREMENTS CAN DETERMINE ALLOWED** THICKNESS(ES)
- OPTICAL VERSUS ELECTRICAL PERFORMANCE TRADE OFF
- COST, POST PROCESSING SPEED, COATING STRESS AND DURABILITY ARE FACTORS
- COATING ENVIRONMENTAL REQUIREMENTS, e.g. TEMPERATURE CYCLING, CAN INFLUENCE CHOICE

# **DETERMINING THE RESISTIVITY "WELL"**

- NOW THAT THE TYPE OF DEPOSITION PROCESS, STARTING MATERIAL, DETERMINE THE INFLUENCE OF OXYGEN FLOW RATE/PARTIAL PRESSURE SUBSTRATE TEMPERATURE AND ITO THICKNESS HAVE BEEN SELECTED, ON (SURFACE) RESISTIVITY
- (POWER SETTING) ADD OXYGEN UNTIL CHAMBER PRESSURE JUST BEGINS AT LOW CHAMBER PRESSURE, WITH A CONSTANT DEPOSITION RATE TO RISE, (OPEN SHUTTER, CHANGE MONITOR CHIP), DEPOSIT A SAMPLE **UNTIL DESIRED THICKNESS IS ACHIEVED**
- IF POSSIBLE, CLOSE SHUTTER, CHANGE CHIP, INCREMENT OXYGEN FLOW RATE AND REPEAT DEPOSITION STEP
- OTHERWISE, BREAK VACUUM REMOVE PART, RELOAD CHAMBER AND REPEAT DEPOSITION STEP AT NEW OXYGEN FLOW RATE
- AFTER SEVERAL DEPOSITIONS AT HIGHER AND LOWER OXYGEN FLOW RATES, PLOT MEASURED RESISTIVITY VERSUS OXYGEN FLOW RATE TO **DETERMINE "WELL"**

TARGET:

90 wt. % In203 / 10 wt. % SnO2

Date: 04-09-96

SUBSTRATE:

Glass Slide

**CONDITIONS:** 

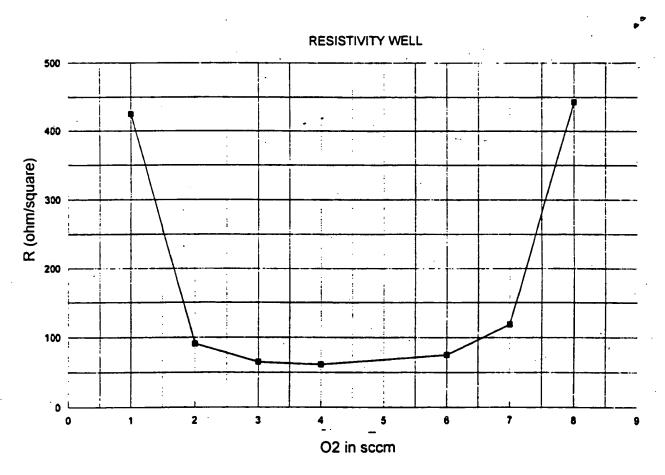
no heat

power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 - 1.9 microns

O2 (sccm)	1	2	3	4	. 6	7	8
R (ohms/square)	425	91.3	64.9	61.05	75	119	443
%T vis (Luminous)	66.8	80.6	84.9	87.1	87.8	86.3	83.3
thickness (nm, slide)	102.6	96.3	107.5	94.3	93.3	99.9	100.5
rho (x1.0E-4 ohm-cm)		8.8	7.0	5.8	7.0	11.9	44.5



■ Surface Resistivity

**TARGET:** 

90 wt. % In203 / 10 wt. % SnO2

Date: 04-09-96

SUBSTRATE:

Glass Slide

**CONDITIONS:** 

no heat

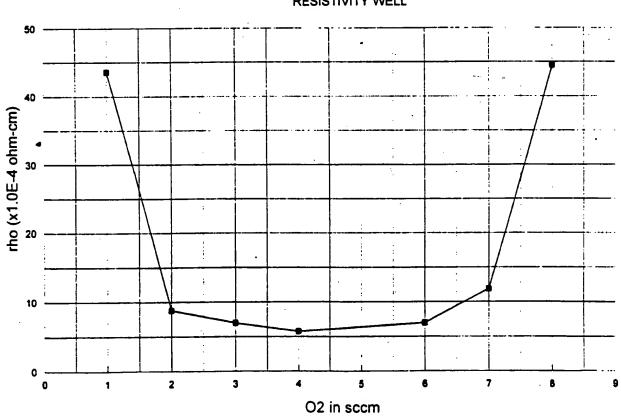
power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 – 1.9 microns

O2 (sccm)	1	2	3	4	6	7	8
R (ohms/square)	425	91.3	64.9	61.1	75	119	443
%T vis (Luminous)	66.8	80.6	84.9	87.1	87.8	86.3	83.3
thickness (nm, slide)	102.6	96.3	107.5	94.3	93.3	99.9	100.5
rho (x1.0E-4 ohm-cm)	43.6	8.8	7.0	5.8	7.0	11.9	44.5





■ Volume Resistivity

Daalanda Losetol

# SELECTING OPTICAL VERSUS ELECTRICAL PERFORMANCE

- ABSORPTANCE OF COATINGS DEPOSITED TO DETERMINE RESISTIVITY DETERMINE SPECTRAL TRANSMITTANCE, REFLECTANCE AND
- APPLICATION, e.g., LUMINOUS TRANSMITTANCE, FOR EACH SAMPLE AND PLOT VERSUS OXYGEN FLOW RATES CALCULATE INTEGRATED OPTICAL VALUES OF INTEREST TO
- FROM PLOTS OF SPECTRAL AND INTEGRATED OPTICAL VALUES, AND RESISTIVITY, SELECT FLOW RATE (PRESSURE) FOR PROCESS WHICH OPTIMIZES COMPROMISE AMONG REQUIREMENTS

TARGET:

90 wt. % In203 / 10 wt. % SnO2

Date: 04-03-96

SUBSTRATE:

Glass Slide

**CONDITIONS:** 

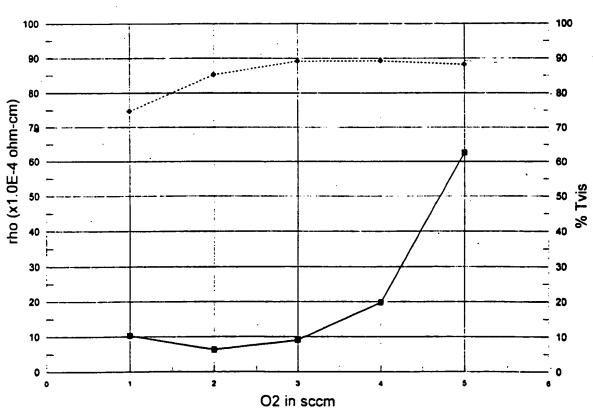
no heat

power .50 KW

speed 5.75 inch/min.total flow 50 sccm pressure 2.0 microns

O2 (sccm)	1	2	3	4	5
R (ohms/square)	102	56.1	67	147.5	492
%T vis (Luminous)	74.7	85.3	89.2	89.3	88.2
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	10.3	6.3	9.1	19.8	62.6

#### RESISTIVITY WELL



■ Volume Resistivity

**+** Luminous Transmittance

**TARGET:** 

90 wt. % In203 / 10 wt. % SnO2

Date: 04-03-96

SUBSTRATE:

**ICI 725 PET** 

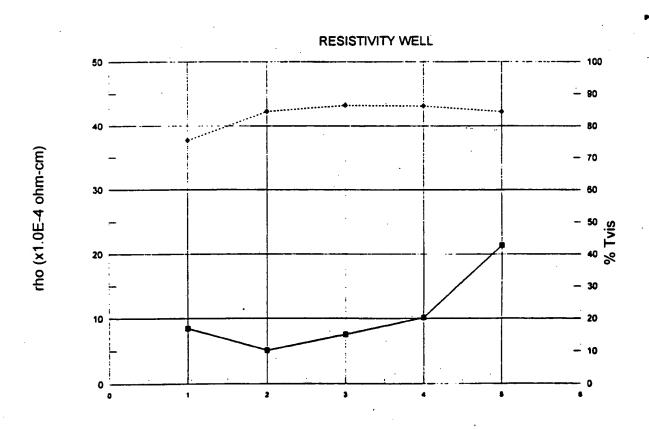
**CONDITIONS:** 

no heat

power .50 KW

speed 5.75 inch/min. total flow 50 sccm pressure 2.0 microns

O2 (sccm)	1	2	3	4	5
R (ohms/square)	83.9	45.2	55.6	75.7	168.3
%T vis (Luminous)	75.5	84.6	86.5	86.3	84.5
thickness (nm, slide)	100.9	113.1	135.8	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.5	5.1	7.6	10.1	21.4



O2 in sccm

■ Volume Resistivity

**♦ Luminous Transmittance** 

TARGET:

90 wt. % In203 / 10 wt. % SnO2

Date: 04-03-96

SUBSTRATE:

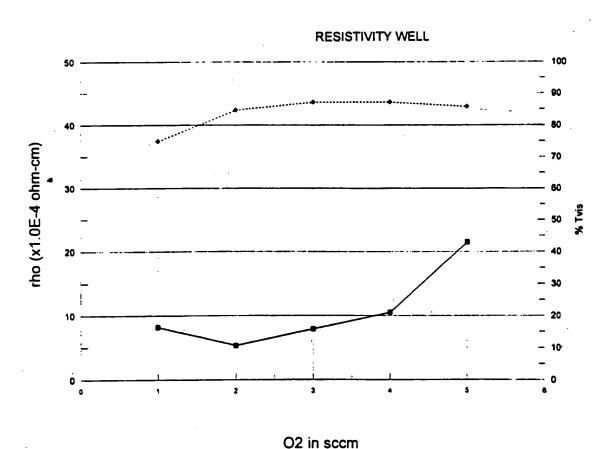
Hardcoat PET

**CONDITIONS:** 

no heat

power .50 KW speed 5.75 inch/min. total flow 50 sccm pressure 2.0 microns

O2 (sccm)	1	2	3	. 4	5
R (ohms/square)	81.5	46.9	58.2	78.4	168.9
%T vis (Luminous)	74.9	84.7	87.2	87.2	85.8
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.2	5.3	7.9	10.5	21.5



■ Volume Resistivity

**♦ Luminous Transmittance** 

#### TIN OXIDE CERAMIC TARGET

TARGET:

98 wt. % SnO2 / 2 wt.% Sb203

Date: 04-09-96

SUBSTRATE:

**ICI 725 PET** 

**CONDITIONS:** 

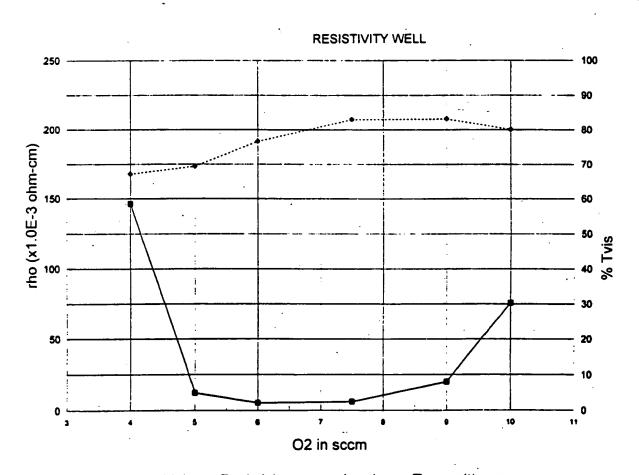
no heat

power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 - 1.9 microns

O2 (sccm)	4	5	6	7.5	9	10
R (ohms/square)	4710	420	183	214	714	3000
%T vis (Luminous)	67.2	69.4	76.6	83	83.2	80.1
thickness (nm, slide)	311	298.0	298.7	294.3	283.1	252.6
rho (x1.0E-3 ohm-cm)	146.5	12.5	5.5	6.3	20.2	75.8



♦ Luminous Transmittance

#### Zinc TIN OXIDE CERAMIC TARGET

**TARGET:** 

98 wt. % ZnO / 2 wt.% Al203

Date: 04-09-96

SUBSTRATE:

**ICI 725 PET** 

**CONDITIONS:** 

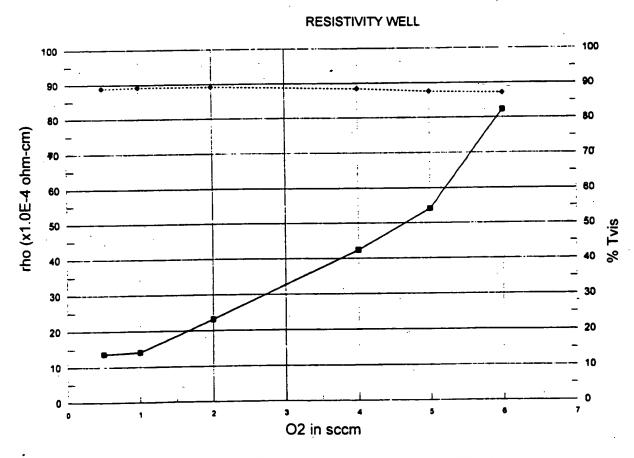
no heat

power .50 KW speed 5.75 inch/r

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 - 1.9 microns

O2 (sccm)	0.5	1	2	4	5	6
R (ohms/square)	124.4	120.9	126.3	211	295	415
%T vis (Luminous)	88.9	89.2	89.2	88.4	87.5	87.1
thickness (nm, slide)	109.9	116.8	183.0	200.9	183.5	198.4
rho (x1.0E-4 ohm-cm)		14.1	23.1	42.4	54.1	82.3



**♦ Luminous Transmittance** 

### MINIMIZING ABSORPTION

- CALCULATE SPECTRAL ABSORPTION COEFFICIENTS FROM MEASURED DATA ON RESISTIVITY "WELL" SAMPLES
- WAVELENGTH WITH OXYGEN FLOW RATE AS A PARAMETER PLOT SPECTRAL ABSORPTION COEFFICIENTS VERSUS
- FOR APPLICATIONS WHERE A SINGLE WAVELENGTH IS DOMINATE PLOT THAT ABSORPTION COEFFICIENT VERSUS FLOW RATE
- SELECT FLOW RATE FOR PROCESS WHICH MINIMIZES ABSORPTION COEFFICIENT NEAR RESISTIVITY MINIMUM

TARGET:

90 wt. % In203 / 10 wt.% SnO2

Date: 04-09-96

SUBSTRATE:

Glass Slide

**CONDITIONS:** 

no heat

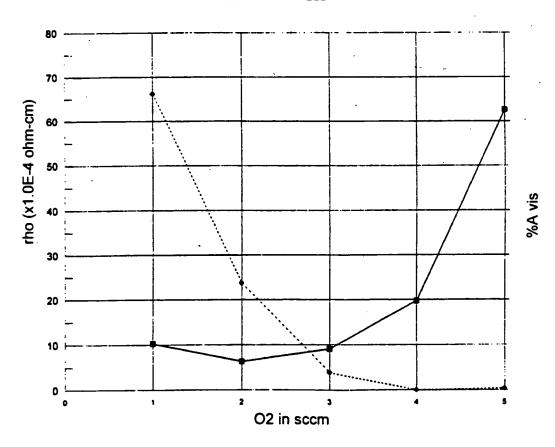
power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 – 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	102	56.1	67	147.5	492
%T vis (Luminous)	74.7	85.3	89.2	89.3	88.2
thickness (nm, slide)	100.9	113.1	135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	10.3	6.3	9.1	19.8	62.6
%A vis (Luminous)	13.24	4.75	0.78	0	0.08

#### **RESISTIVITY WELL**



■ Volume Resistivity

◆ Luminous Absorptance

TARGET:

90 wt. % In203 / 10 wt.% SnO2

Date: 04-09-96

SUBSTRATE:

**ICI 725 PET** 

**CONDITIONS:** 

no heat

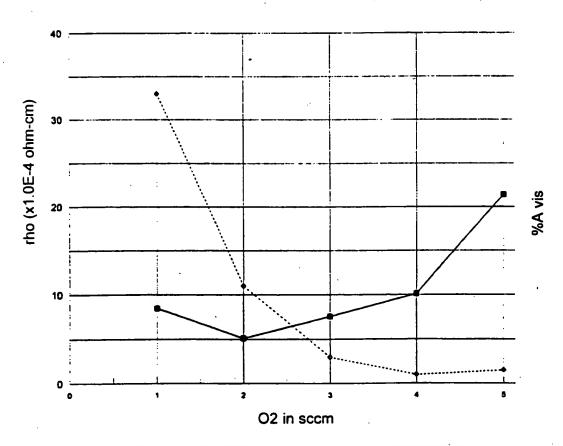
power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 – 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	83.9	45.2	55.6	75.7	168.3
%T vis (Luminous)	75.5	84.6	86.5	86.3	84.5
thickness (nm, slide)	100.9	113.1	135.8	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.5	5.1	7.6	10.1	21.4
%A vis (Luminous)	13.2	4.4	1.2	0.4	0.6

#### **RESISTIVITY WELL**



■ Volume Resistivity

♦ Luminous Absorptance

TARGET:

90 wt. % In203 / 10 wt.% SnO2

Date: 04-09-96

SUBSTRATE:

Hardcoat PET

**CONDITIONS:** 

no heat

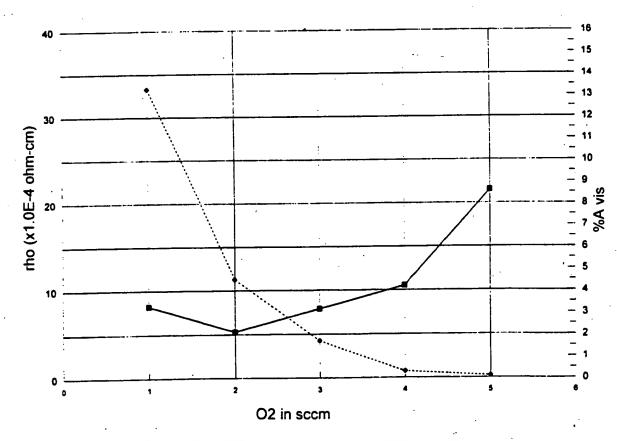
power .50 KW

speed 5.75 inch/min. total flow 50 sccm

pressure 1.8 - 1.9 microns

O2 (sccm	1	2	3	4	5
R (ohms/square)	81.5	46.9	58.2	78.4	168.9
%T vis (Luminous)	74.9	84.7	87.2	87.2	85.8
thickness (nm, slide)	100.9	113.1	.135.7	133.9	127.3
rho (x1.0E-4 ohm-cm)	8.2	5.3	7.9	10.5	21.5
%A vis (Luminous)	13.3	4.5	1.7	0.3	0.1

#### RESISTIVITY WELL



♦ Luminous Absorptance.

### ITO PROCESS EXAMPLES

# **DC MAGNETRON SPUTTERING**

- REACTIVE PROCESS FROM 90% In / 10% Sn (WEIGHT) TARGET
- SUBSTRATE PET (POLYETHYLENE TEREPHTHALATE) PLASTIC FILM
- TYPICAL ROLL COATER PROCESS PARAMETERS:
- 1. CHAMBER PRESSURE 3.7 MICRONS (3.7 MILLITORR)
- 2. FLOW RATES 265 SCCM ARGON, 144 SCCM OXYGEN
  - 3. ITO THICKNESS NEAR 100 NM
- 4. TARGET AREA = 75 IN<sup>2</sup> = 484 CM<sup>2</sup>, SO FOR TARGET POWER OF 2000 WATTS POWER DENSITY = 4.1 WATTS
- 5. DEPOSITION RATE = 6.5 NM

SEC

6. SUBSTRATE TEMPERATURE - NEAR ROOM TEMPERATURE (COOLED DRUM)

### **ITO PROCESS EXAMPLES**

# DC MAGNETRON SPUTTERING - REACTIVE PROCESS

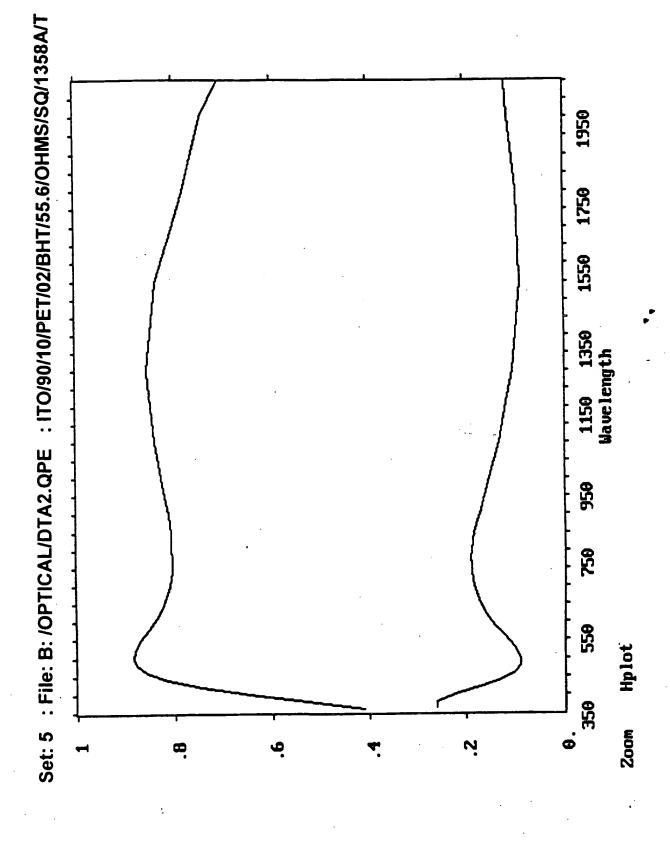
RESISTIVITY VERS	VERSUS OXYGEN FLOW RATE WITH CORRESPONDING (TIES:	W RATE WITH CO	ORRESPONDING
OHMS/SQUARE	O <sub>2</sub> RATE (SCCM)	FOMINOUS % T	LUMINOUS % T LUMINOUS % R
74	141	78.5	18.6
192	144	79.0	19.2
232	147	80.7	16.9
370	148	81.5	16.3
555	149	82.0	15.6
1428	150	83.4	14.4
2000	155	87.4	11.2

15.7

### **ITO PROCESS EXAMPLES**

# DC MAGNETRON SPUTTERING

- SEMIREACTIVE PROCESS FROM 90%  $\ln_2 O_3$  / 10%  $\mathrm{SnO}_2$  (WEIGHT) **CERAMIC TARGET**
- SUBSTRATES PET FILM AND GLASS SLIDES
- TYPICAL IN-LINE COATER PROCESS PARAMETERS:
- 2. FLOW RATES 45 49 SCCM ARGON 1 5 SCCM OXYGEN I. CHAMBER PRESSURE - 2 MICRON (2 MILLITORR)
  - 3. ITO THICKNESS NEAR 130 NM
- 4. TARGET AREA = 48 IN<sup>2</sup> = 310 CM<sup>2</sup> SO FOR TARGET POWER OF 500 WATTS POWER DENSITY = 1.6 WATTS
- 5. DEPOSITION RATE =  $\frac{3 \text{ NM}}{2 \text{ NM}}$ 
  - SEC
- 6. SUBSTRATE TEMPERATURE NEAR ROOM TEMPERATURE



#### **10 PROCESS EXAMPLE**

### THERMAL EVAPORATION

- REACTIVE PROCESS FROM In METAL
- SUBSTRATES GLASS AND OTHER TEMPERATURE TOLERANT MATERIALS
- TYPICAL BELL JAR COATER PROCESS PARAMETERS:
- 1. CHAMBER PRESSURE 1 TO 3 MILLITORR
- 2. FLOW RATE MAINTAIN OXYGEN PRESSURE
  - 3. IO THICKNESS 100 NM TO 143 NM
- 4. RATE 0.1 NM SEC
- 5. SUBSTRATE TEMPERATURE 230 °C

### 10 PROCESS EXAMPLE

## THERMAL EVAPORATION

RESISTIVITY VERSUS OXYGEN PRESSURE:

RHO (MILLIOHMS-CM) PRESSURE (MILLITORR)	1.0	2.0	3.0
RHO (MILLIOHMS-CM) PR	0.38	0.34	0.55
THICKNESS (NM)	142.0	105.0	2.66
OHMS/SQUARE	27.0	32.8	54.8

### THERMAL EVAPORATION

OPTICAL PERFORMANCE:

= 88.1% = 8.8% = 3.1% = 1.91REFRACTIVE INDEX AT 550 NM **-UMINOUS TRANSMITTANCE** LUMINOUS ABSORPTANCE LUMINOUS REFLECTANCE (AND SCATTERING)

 $= 8.2 \times 10^{-3}$ **EXTINCTION COEFFICIENT AT 550 NM** 

ELECTRICAL PERFORMANCE:

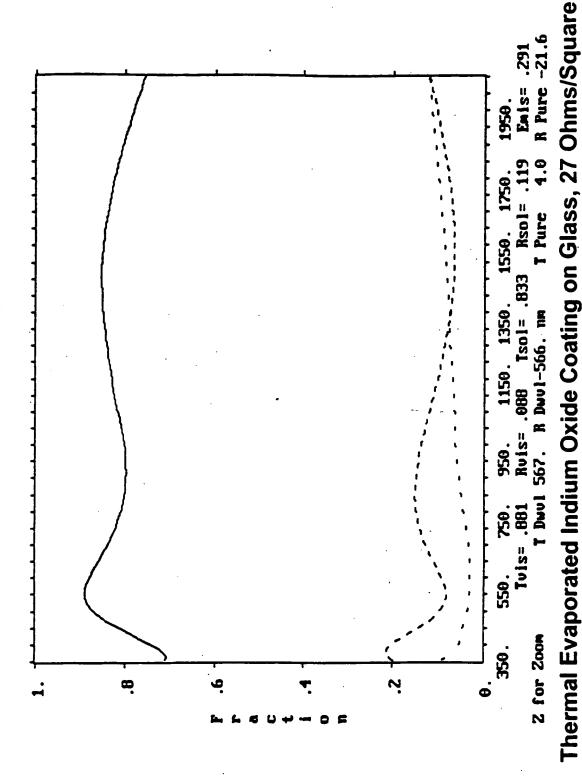
SURFACE RESISTIVITY
THICKNESS
RESISTIVITY
ELECTRON DENSITY
MOBILITY

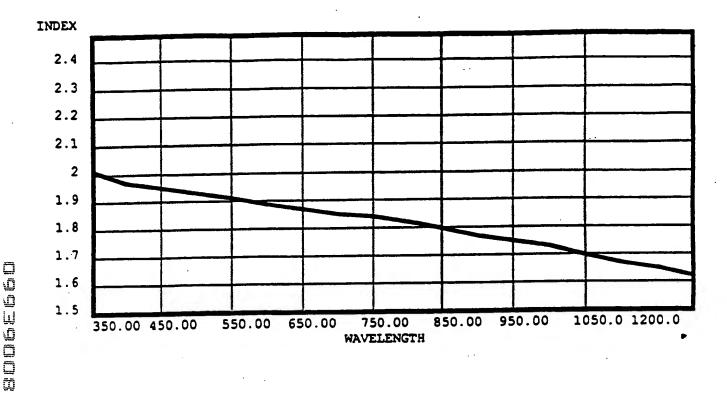
= 27.0 OHMS/SQUARE = 142.3 NM

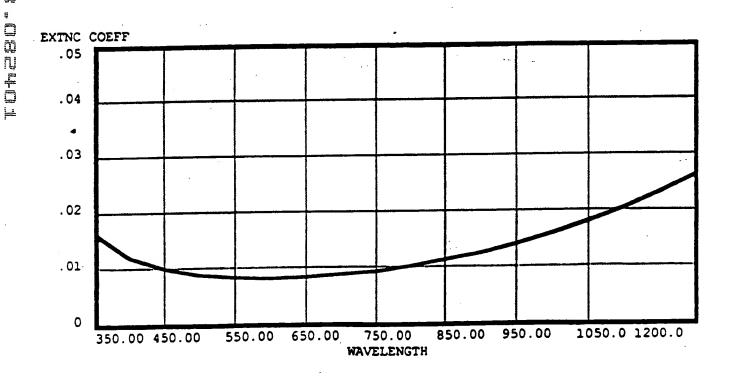
 $= 3.8 \times 10^{-4} \text{ OHMS} - \text{CM}$  $= 9.2 \times 10^{20} \text{ CM}^{-3}$ 

 $= 18 \frac{\text{CM}^2}{\text{VOLT SEC}}$ 

### **10 PROCESS EXAMPLE**







Optical Constant for Evaporated Indium Oxide Coating on Glass 1 mtorr Q<sub>2</sub>, 27 Ohms/Square (From C. I. Bright, 36<sup>th</sup> SVC Tech. Con. Proc., (1993) 63 – 67)

### **ZrN PROCESS EXAMPLE**

# DC MAGNETRON SPUTTERING

- REACTIVE PROCESS FROM Zr METAL TARGET
- SUBSTRATE-CORNING 7059 GLASS AND SILCON WAFERS
- TYPICAL IN-LINE COATER PROCESS PARAMETERS
- 1. CHAMBER PRESSURE = 0.2 0.3 Pa
- 2. FLOW RATES = 100 sccm ARGON, 15 25 sccm NITROGEN
  - 3. ZrN THICKNESS  $\sim$  18 390 nm
- 4. TARGET POWER = 1400 2400 WATTS 5. TARGET/SUBSTRATE DISTANCE = 120 mm 6. DEPOSITION RATE = 6 nm/sec
- 7. SUBSTRATE TEMPERATURE = 150 °C, 300 °C

(Data from M Veszelei et al, Optical Constants and Drude Analysis of Sputtered ZrN Films, Applied Optics, 33,10 1994)

## ZrN PROCESS EXAMPLE

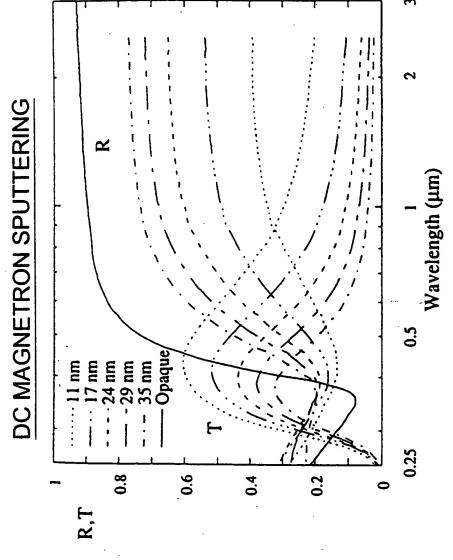
# DC MAGNETRON SPUTTERING

REFLECTANCE AS A FUNCTION OF NITROGEN FLOW RATE

N <sub>2</sub> FLOW RATE (SCCM)	REFLECTANCE (%) MINIMUM 18% (305 nm)	REFLECTANCE (%) AT 2 um	REFLECTANCE (%) AT 10 um
	*15% (~420 nm)	%98*	%6 <del>*</del>
	8% (355 nm)	91%	94%
	9% (355 nm)	%06	94%

(Data From M. Veszelei et al, A.O., 33 10, 1994 and \*Data From A. Spencer et al, Solar Energy Material, 18,1988)

### **ZrN PROCESS EXAMPLE**



(From M. Veszelei et al, Optical Characterization of Sputtered Semi-Transparent ZiN Films, Reflectance and Transmittance for Various Thickness of ZrN Films. Optical Materials 2, 1993)

# RF MAGNETRON SPUTTERING

- REACTIVE PROCESS FROM TI METAL TARGET
- SUBSTRATE-CORNING 7059 BOROSILICATE GLASS
- R&D COATER
- 8. CHAMBER PRESSURE = 0.67 Pa
- 9. GAS MIXTURE = ARGON WITH 8% NITROGEN
  - ). THICKNESSES = 4 76 nm
- TARGET POWER = 100 WATTS
- 2. DEPOSITION RATE = 10.6 nm/min 3. SUBSTRATE TEMPERATURE = 400 °C

(Data from M. Kawamura et al, Characterization of Thin, Transparent and Conductive TIN FIIms, JVST A, 16 (1) 1998)

#### HOTOUGO TOOUGH

## TIN PROCESS EXAMPLE

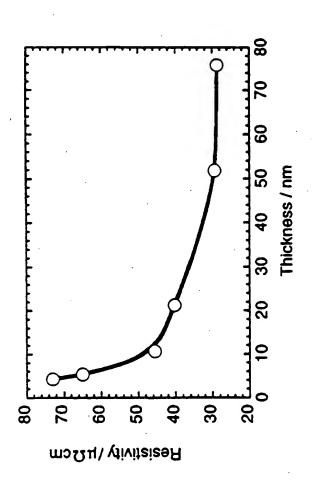
# RF MAGNETRON SPUTTERING

# ELECTRICAL AND OPTICAL PROPERTIES OF TIN THIN FILMS

Thickness (nm)	Sheet resistance (Ω/⊡)	Resisticity (μΩ cm)	Tmax (%)
4.2	173	73	79
5.3	123	65	9/
11	43	46	64
21	19	40	47
52	5.7	30	26

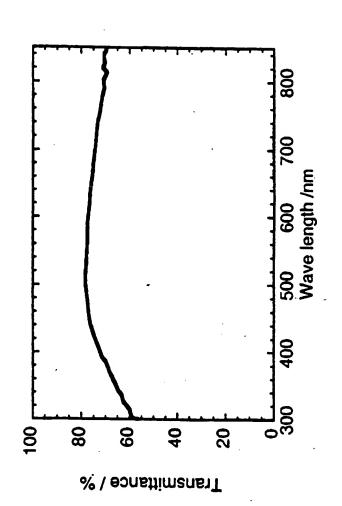
(From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

# RF MAGNETRON SPUTTERING



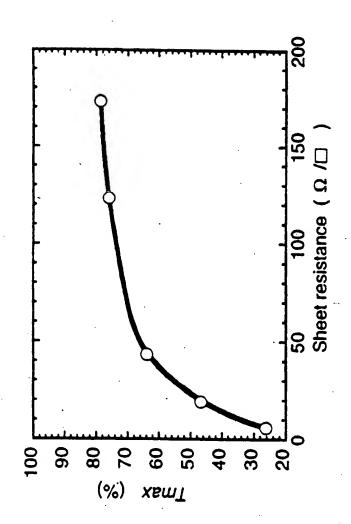
The Resistivity (p) Change With Film Thickness of TiN Films. (From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

# RF MAGNETRON SPUTTERING



Transmission of TiN Film (d=4.2 nm) (Glass Substrate Removed) (From M. Kawamura et al, characterization of TiN Films, JVST A 16 (1) 1998)

# RF MAGNETRON SPUTTERING



Relationship Between Sheet Resistance and Maximum Transmission (at ~500 nm) of TiN Films.

(From M. Kawamura et al, Characterization of TiN Films, JVST A 16 (1) 1998)

### LOPSCOS BOOKEDS

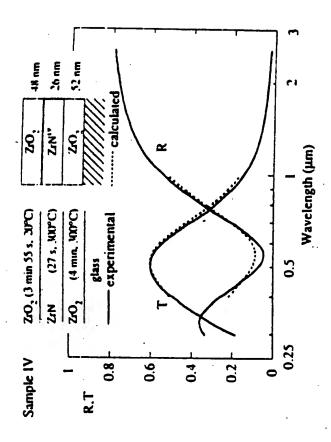
# KEY COATING PARAMETERS BY APPLICATION FUNCTION

AR			. <b>×</b>	×	
Heat Mirror AR			×		×
Heater Antistatic	×		×		
Heater	×		×		·
EMI Shield		×	<b>×</b>	** · •	
Transparent Electrodes		× (e)	<b>ω</b>		
Parameter	Resistance (Ohms)	Surface Resistivity (Ohms/Square)	Visible Transmittance	Visible Reflectance	Infrared Reflectance
					•

### **APPLICATION EXAMPLES**

#### HEAT MIRROR

### OPTICALLY ENHANCED ZrN

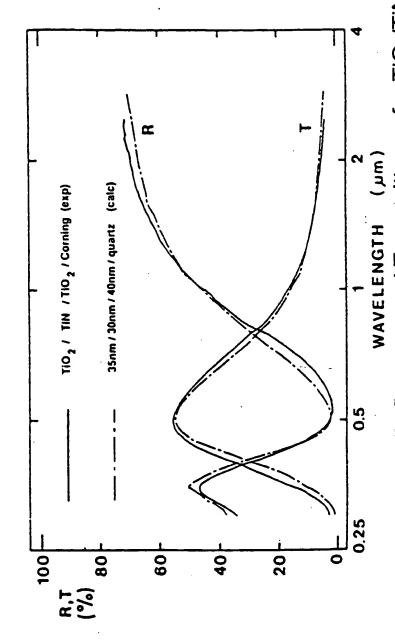


Calculated and Measured Reflectance and Transmittance for ZrO<sub>2</sub>/ZrN/ZrO<sub>2</sub>. (From K. Andersson et al, ZrN Based Transparent Heat Mirror Coatings, Solar Energy Mat. 32, 1994)

### APPLICATION EXAMPLES

#### HEAT MIRROR

### OPTICALLY ENHANCED TIN



Calculated and Measured Reflectance and Transmittance for TiO<sub>2</sub>/TiN/TiO<sub>2</sub>. (From Y. Claesson et al, Characterization of TiN-Based Solar Control Coatings, Solar Energy Mat. 20, 1990)

# RESISTIVITY ANTI – ICING HEATER FOR TV AND LASER WINDOW

#### REQUIREMENTS

- Power Dissipation Of 1.5 Watts/in<sup>2</sup> From 28 Volt Source
- Coated Window Transmittance of

T visible > 84% From 525 nm 625 nm T average > 83% Between 700 nm 900 nm

T laser > 82% At 1070nm

- Laser Damage Resistant
- Durability to MIL-C-48497

APPLICATION TYPE: Resistive Heater

TRADEOFF PRIORITIES:

Electrical Performance (resistance)

2. Optical Performance 3. Laser Damage Resistance

4. Durability

- Coating Surface Resistivities Between 10.6 And 14.2 Ohms/Square Yields Correct Resistance For Proper Heating
- Two Layer ITO/SIO<sub>2</sub> Coating Design Meets Optical Requirements
- Design Adjusted For Electric Field Control At Interfaces
- Durability Met By Materials Choice And Deposition Process

## **MEASURED TCO PERFORMANCE**

Heater Resistance = 7.9 Ohms (11.3 OHMs/Square)

Window Transmittance

T visible 525nm - 625nm = 88%

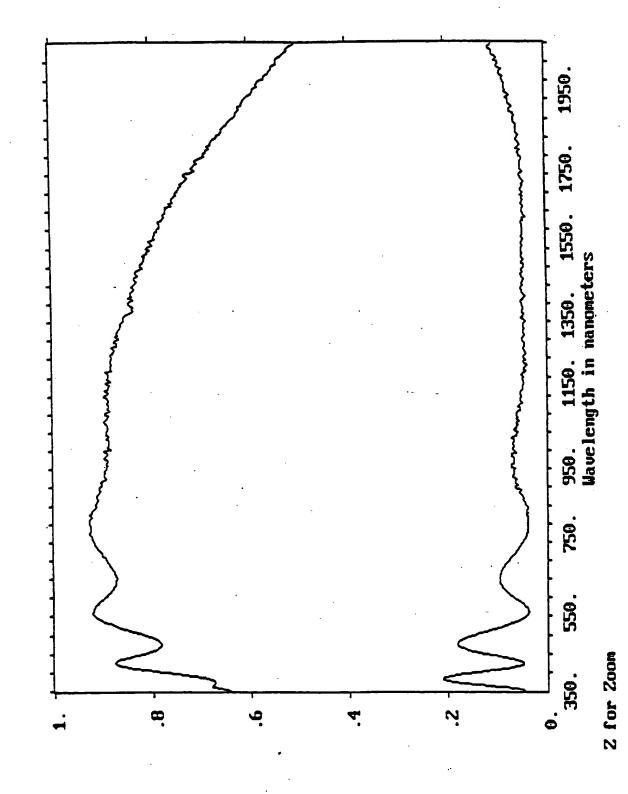
T average 700nm – 910nm = 92%

T laser 1070nm = 89%

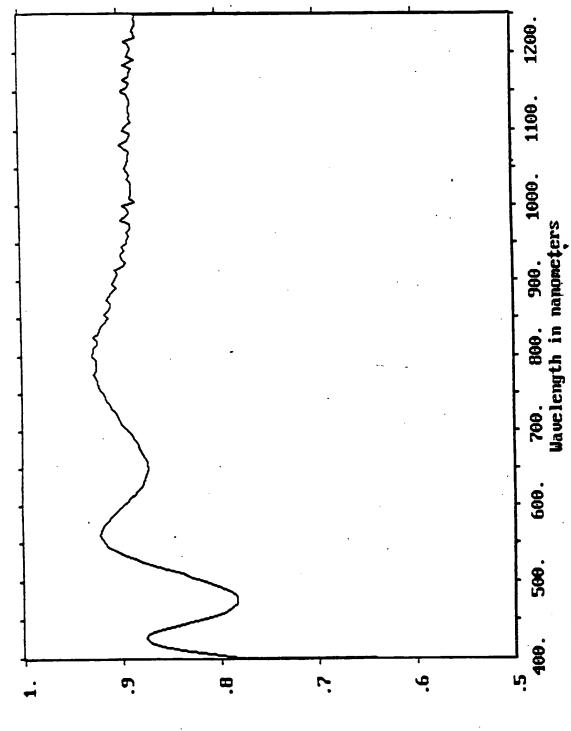
Passed Laser Damage Testing At 22.5 to  $36.0~\mathrm{MW/cm}^2$ 

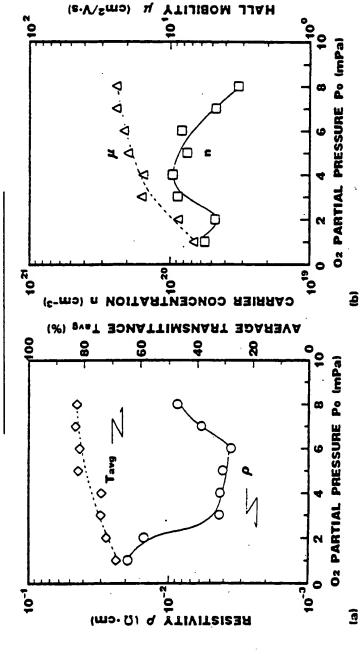
Passed Durability Tests Of MIL-C-48497

RESISTIVITY ANTI-ICING HEATER FOR TV AND LASER WINDOW



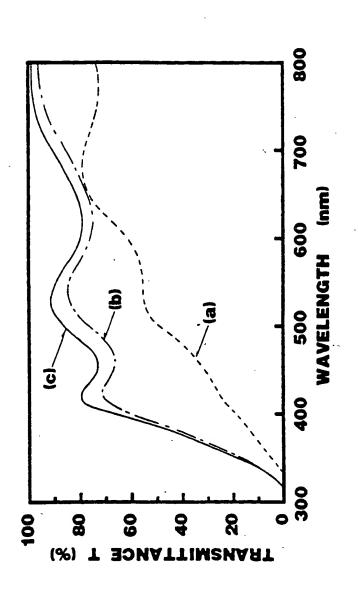
## RESISTIVITY ANTI-ICING HEATER FOR TV AND LASER WINDOW





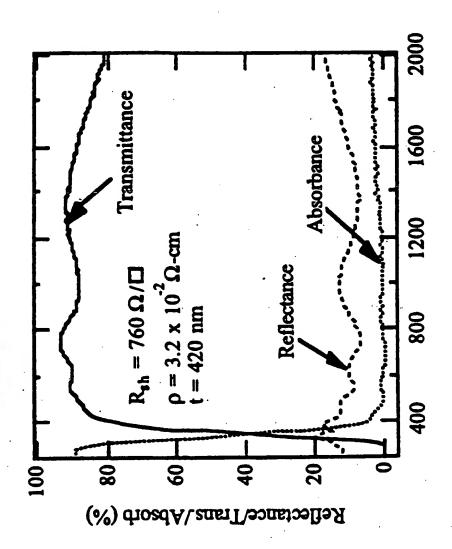
Mobility (∆) and Carrier Concentration (□) as Functions of the Oxygen Partial (a) Resistivity (o) and Average Transmittance in the Visible Range (◊), (b) Hall (From T. Minami et al, Preparation of Transparent Zinc Stannate Conducting Films, JVST A, 13, 3 1995) Pressure for Zinc Stannate Films Prepared at RT (~140°C)

### **NEW TCO MATERIALS**

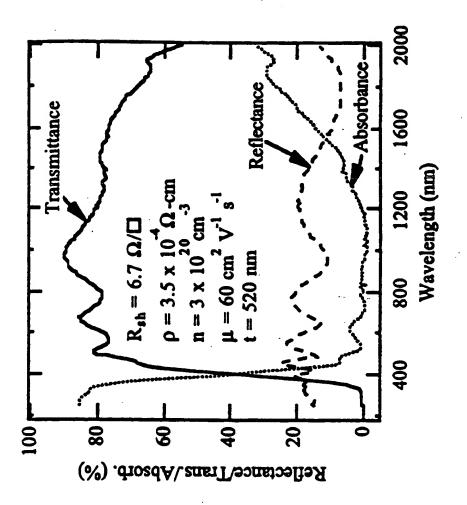


Transmission Spectra for Zinc Stannate Films Deposited with Oxygen Partial Pressures of 0 Pa [curve (a), Film Thickness of 470nm], 2 mPa [curve (b), 310 nm] and 5 mPa [curve (c), 300 nm].

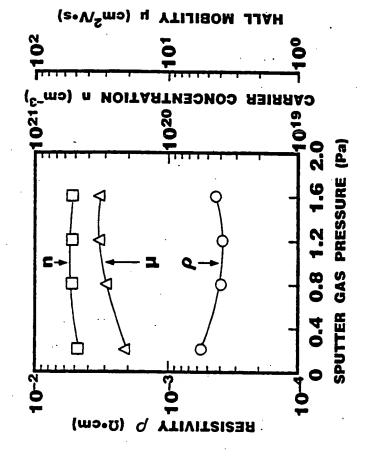
(From T. Minami et al, Properties of Transparent Zinc-Stannate Conducting Films, JVST A, 13, 3 1995)



(From X. Wu et al, Properties of Transparent Conducting Cd<sub>2</sub>SnO<sub>4</sub> and Zn<sub>2</sub>SnO<sub>4</sub>, 39<sup>h</sup> SVC, 1996) Transmittance, Reflectance, and Absorbance for a Zn<sub>2</sub>SnO<sub>4</sub> Film.

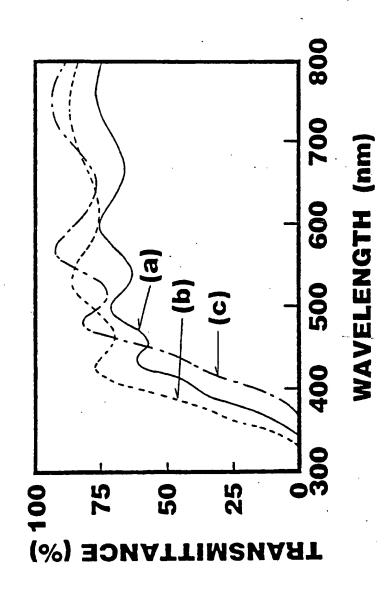


(From X. Wu et al, Properties of Transparent Conducting Cd<sub>2</sub>SnO<sub>4</sub> and Zn<sub>2</sub>SnO<sub>4</sub>, 39<sup>th</sup> SVC, 1996) Transmittance, Reflectance, and Absorbance for a Cd<sub>2</sub>SnO<sub>4</sub> Film.



Resistivity (o), Carrier Concentration (□) and Hall Mobility (△) as a Function (From T. Minami et al, New Transparent Conducting Zn₂ln₂O₅Thin Films, ICMCTF, 1995) of Sputter Gas Pressure for Zn<sub>2</sub>ln<sub>2</sub>O<sub>5</sub> Films (Substrate ~140°C).

### **NEW TCO MATERIALS**

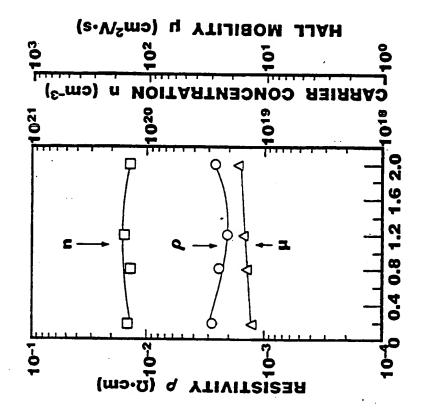


Conditions; (a) RT Substrate (~140°C), Ar only, (b) 350°C Substrate, Ar only, Optical Transmission for Zn<sub>2</sub>ln<sub>2</sub>O<sub>5</sub> Films Prepared with Different (c) RT Substrate ( $\sim 140^{\circ}$ C), Ar 20% + O<sub>2</sub>.

(From T. Minami et al, New Transparent Conducting Zn₂ln₂O₅Thin Films, ICMCTF, 1995)

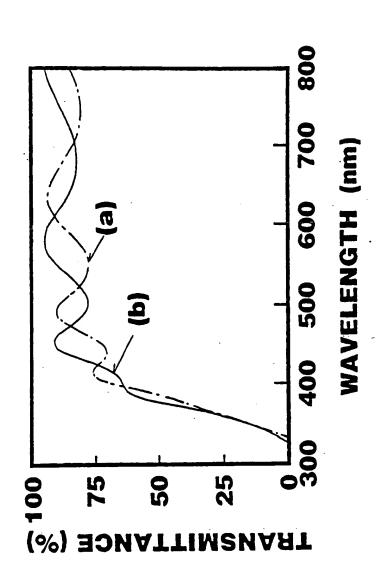
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#### **NEW TCO MATERIALS**



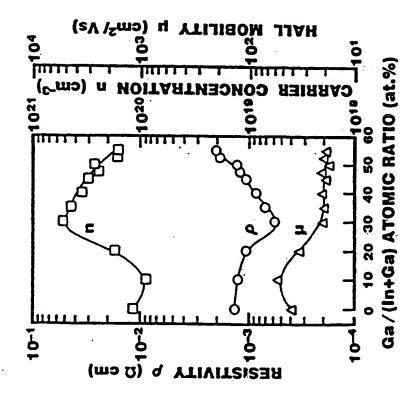
Resistivity (o), Carrier Concentration (□) and Hall Mobility (△) as a Function of Sputter Gas Pressure for MgIn<sub>2</sub>O<sub>4</sub> Films (RT Substrate ~140°C). (From T. Minami et al, New Transparent Conducting Zn₂ln₂O₅Thin Films, ICMCTF, 1995)

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Optical Transmission of Mgln<sub>2</sub>O<sub>4</sub> Films [Ar pressure (a) 0.8 Pa, (b) 1.2 Pa]. (From T. Minami et al, New Transparent Conducting Mgln<sub>2</sub>O<sub>4</sub> Thin Films, ICMCTF, 1995)

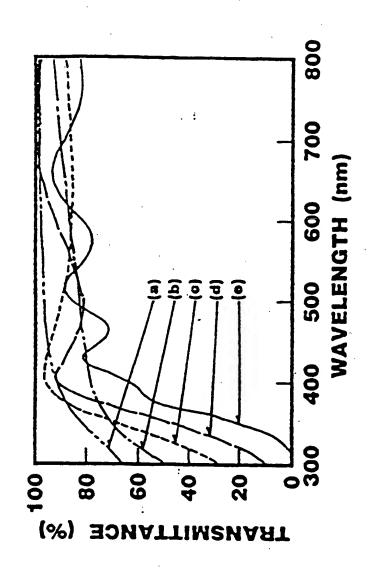
### **NEW TCO MATERIALS**



Resistivity (o), Carrier Concentration (□) and Hall Mobility (△) as Functions of Ga Content for Ga<sub>2</sub>O<sub>3</sub>-In<sub>2</sub>O<sub>3</sub> Films Prepared at RT (~180°C). (From T. Minami et al, Preparation of Highly Transparent Films, JVST A, 15, 3 1997)

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### **NEW TCO MATERIALS**



Transmittance of (Ga,In)₂O₃ Films Prepared at RT (~180°C) With Ga Content of 50 at. % and Thickness of (a) 20, (b) 55, (c) 100, (d) 185 and (e) 500 nm. (From T. Minami et al, Preparation of Highly Transparent Films, JVST A, 15, 3 1997)

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## EXCIMER LASER (XeCI @ 308 nm) ABLATION

ELECTRICAL AND OPTICAL PROPERTIES OF ZnO FILMS PREPARED AT SUBSTRATE TEMPERATURE OF 300°C.

	Al-doped ZnO	Ga-doped ZnO
Resitivity (Ω • cm)	1.4X10 <sup>4</sup>	2.7×10 <sup>-4</sup>
Hall mobility (cm2N • s)	45	18
Carrier concentration (cm <sup>-3</sup> )	9.9×10 <sup>20</sup>	1.3x10 <sup>21</sup>
Transmittance (%)	06	06
Film thickness (nm)	150	230
Dopant in target (wt%)	1.0	7.0

(From K Imaede et al, Highly Conductive and Transparent ZnO :Al Thin Films, Presented at 43rd AVS, 1996)

#### REFERENCES PARTI

SECTION I: FUNDAMENTALS OF CONDUCTIVITY AND THIN FILM OPTICS

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2. W.R. Beam, Electronics of Solids, McGraw-Hill, New York, 1965

H.A. Macleod, Thin-Film Optical Filters, Second Edition, Macmillam Publishing, New York, Adam Hilger Ltd, Bristol

O.S. Heavens, Optical Properties of Thin Solid Films, Dover Publications, New York, 1965

J.L. Vossen and W. Kern, editors, Thin Film Processes II, Academic Press, Inc. Boston, 1991

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7. K.L. Chopra, S. Major and K. Pandya, "Transparent conductors – a status review", Thin Solid Films, 102, 1-46 (1983)

8. J.L. Vossen, "Transparent conducting films", Physics of Thin Films, Vol. 9, G. Hass, M.H. Francombe and R.W. Hoffman (editors). pp 1-71, Academic Press, Inc. New York (1977)

## SECTION II: TCC FUNCTION AND PERFORMANCE IN APPLICATIONS

1. C.M. Lampert, "Heat mirror coatings for energy conserving windows", Solar Energy Mat. 6, 1 (1981) 2. J.C.C. Fan, "Sputter films for wavelength-selective applications", Thin Solid Films, 80, 125 1981

## SECTION III: MAJOR DEPOSITION METHODS FOR TCC

1. I. Maissel and R. Glang, Editors, Handbook of Thin Film Technology, McGraw-Hill Book Co., New York (1970)

## SECTION V: DEVELOPING A TCO DEPOSITION PROCESS

SECTION IV: IMPORTANT PROCESS PARAMETER FOR TRANSPARENT CONDUCTIVE OXIDES

## SECTION V: DEVELOPING A TCO DEPOSITION PROCESS

**PROPERTIES** SECTION VI: TCO PROCESS EXAMPLES AND ASSOCIATED COATING 1. D.B. Fraser and H.D. Cook, "Highly conductive transparent films of sputtered Inz. Sn.O3.,", J. Electrochem. Soc., 119, 1368 (1972)

#### REFERENCES **PART II**

SPECIFIC APPLICATION STRATEGY FOR DEVELOPING A TCC TO MEET REQUIREMENTS SECTION VII:

SECTION VIII: APPLICATION EXAMPLES

SECTION IX: SPECIFING AND SELECTING COMMERCIALLY AVAILABLE TCC

SECTION X: ADVANCED TOPICS

T. Minami, Y. Takeda, T. Kakuma, S. Takata and I. Fukuda, "Preparation of highly transparent and conducting Ga<sub>2</sub>O<sub>3</sub> – In<sub>2</sub>O<sub>3</sub> films by DC magnetron sputtering", J. Vac. Sci. Technol. A 15(3) May/Jun 1997

2. K. Tominaza, H. Munabe, N. Umezu, I. Mori, T. Ushiro and I. Nakabayashi, "Film properties of ZnO:Al prepared by co-

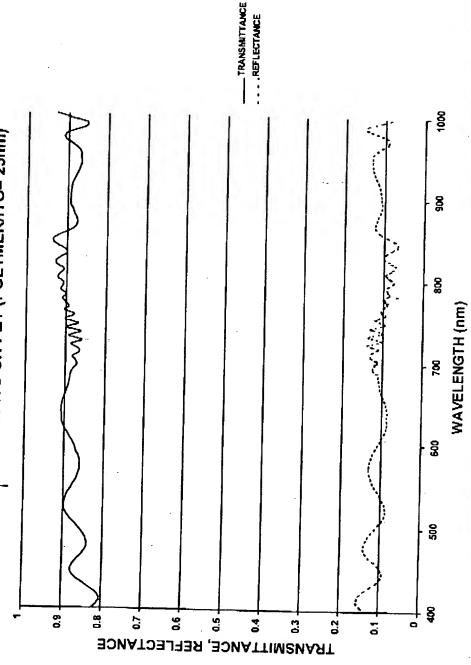
sputtering of ZnO:Al and either Zn or Al targets",

3. X. Wu, W.P. Mulligan and T.J. Coutts, "Electrical and Optical properties of transparent conducting cadmium stannate and zinc stannate thin films prepared by RF sputtering", in Proc. of 39" Annual Technical Conference, Society of Vacuum Coaters", 1996

4. T. Minami, S. Takata, T. Kakuma, and H. Sonohara, "New transparent conducting Mgln<sub>2</sub>O<sub>4</sub> – Zn<sub>2</sub>In<sub>2</sub>O<sub>5</sub> thin films prepared by magnetron

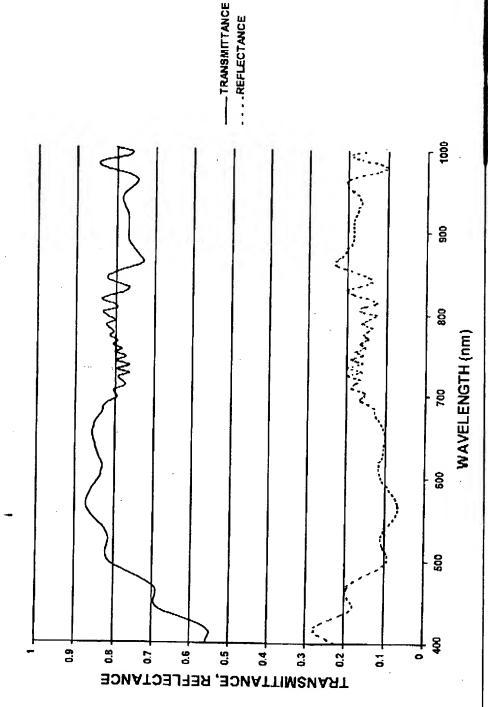
sputtering", Proc. Of ICMCTF, (1995)
5. T. Minami, S. Takata, H. Sato, and H. Sonohara, "Properties of transparent Zinc-stannate conducting films prepared by RF magnetron sputtering", J. Vac. Sci. Technol. A 13(3), May/Jun 1995



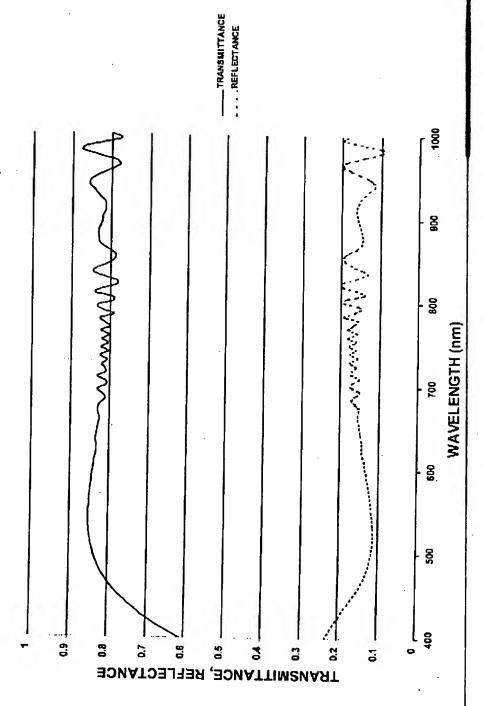


Appendix E

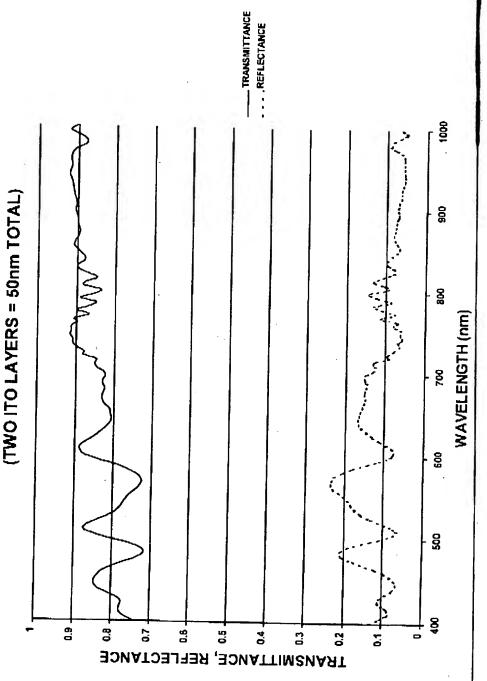
TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO ON PET (POLYMER/ITO= 153 nm)



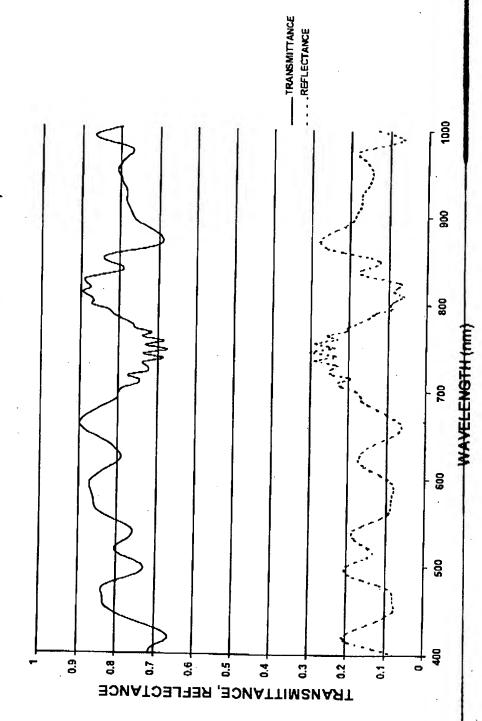
TRANSMITTANCE AND REFLECATNCE OF SEMI-REACTIVELY SPUTTERED ITO ON PET (SINGLE LAYER ITO 134 nm)



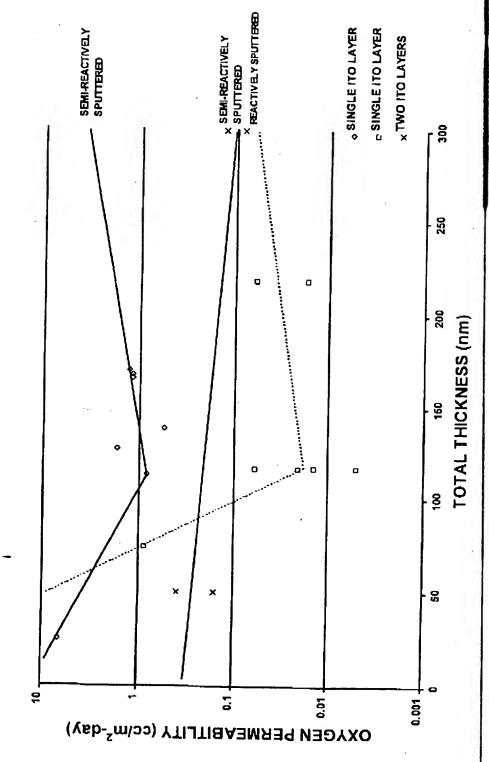
TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY
SPUTTERED ITO/POLYMER ON PET



TRANSMITTANCE AND REFLECTANCE OF SEMI-REACTIVELY SPUTTERED ITO POLYMER ON PET (TWO ITO LAYERS = 299nm TOTAL)



OXYGEN PERMEABILITY VERSUS ITO THICKNESS



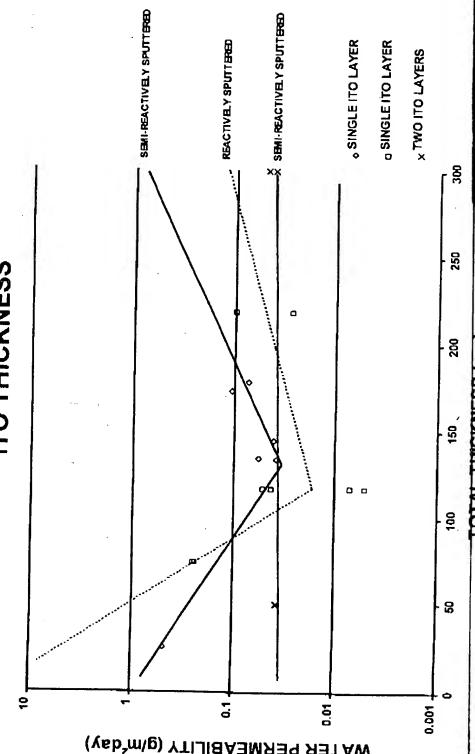
Appendix D

# Experimental Results For ITO Barriers on PET

### Semi-Reactively Sputtered

0.038	0.0246	0.8625
0.0621	0.12	0.2375
~80	~82	98~
6.94	6.64	25.6
31.8	57.48	348.5
218.5	117.05	74.3
	31.8 6.94 ~80 0.0621	31.8 6.94 ~80 0.0621 57.48 6.64 ~82 0.12





# Experimental Results For ITO Barriers on PET

### Semi-Reactively Sputtered

	O <sub>2</sub> Permeance (g/m²-day)	0.827	1.19	0.081	0.156
no lound (indicated the control of t	$H_2O$ Permeance (cc/m <sup>2</sup> -day)	0.038	0.073	0.049	0.036
	Luminoust (%)	84	82	~81	~81
	Rho (x10 <sup>-4</sup> п-ст)	4.685	5.145	5.15	9.4
	Surface Resistivity (ohms/square)	38.3	29.9	17.2	188.4
	Total ITO Thickness (nm)	123.3	172.4	299.2	49.9